COLLISION INTEGRALS FOR THE KNUDSEN NUMBER DEPENDENCE OF THE GROWTH RATE OF DROPLETS IN A SUPERSATURATED VAPOR

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FOREWORD

The research reported herein was conducted at the National Bureau of Standards and at the University of Maryland. The portion of the research pertaining to AEDC was conducted at the Institute for Molecular Physics of the University of Maryland during the period from July 1, 1971 till August 31, 1972 under delivery order F40600-72-C-0002. Air Force project monitor for this project was E. R. Thompson, AEDC (DYR).

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This technical report has been reviewed and is approved.

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ABSTRACT

A method is developed for calculating the mass flux to a liquid droplet surrounded by its pure vapor as a function of the Knudsen number. The Knudsen number K is defined as the ratio of the mean free path to the droplet size. When the mass flux is expanded in terms of the inverse Knudsen number $\alpha = K^{-1}$, we obtain a series of the form

$$\Gamma = \Gamma^{(0)} + \Gamma^{(1)}\alpha + \tilde{\Gamma}^{(2)}\alpha^2 \ln\alpha + \ldots .$$

It is shown that the coefficients are determined by integrals associated with sequences of successive collisions among a number of vapor molecules and the droplet. In particular, we derive the collision integrals for the first three coefficients of the inverse Knudsen number expansion for Γ. These collision integrals bear a close similarity to the collision integrals derived in earlier technical reports for the density dependence of the transport properties of gases. It will be demonstrated in a subsequent technical report that the same method can be used to calculate the aerodynamic force on an object in a gas stream as a function of the Knudsen number.

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For a droplet to be in equilibrium with the surrounding vapor, its rate of vaporization must be equal to the rate at which vapor is condensing onto the surface of the droplet. Such an equilibrium is only possible when the droplet has a very particular critical size [1]. Droplets smaller than the critical size are called "embryos"; they will tend to evaporate and disappear. Droplets larger than the critical size will tend to grow. Nucleation theories are concerned with predicting the rate at which these growing nuclei are created per unit volume. For a review of the theory of nucleation the reader is referred to reference [2].

In this technical report we are concerned with the rate of change of the liquid droplets once formed in the vapor. In particular we shall consider the rate of change of mass of liquid droplets surrounded by the pure vapor. The theory to be presented is valid for droplets formed either by homogeneous or heterogeneous nucleation.

We assume that the average distance between all liquid droplets is significantly larger than both the radius R of the droplets under consideration and the mean free path ℓ of the molecules in the vapor phase. Under these circumstances we may neglect the interaction between different droplets and it is sufficient for the problem of droplet growth to evaluate the net mass flux of vapor molecules to

an individual droplet of radius R and temperature T_L, surrounded by its vapor at temperature T_∞. When the density of the vapor is not too large, this net mass flux can be obtained by solving the Boltzmann equation in the vapor phase, subject to the appropriate boundary conditions at the surface of the droplet.

The mass flux to the droplet will in general depend on the ratio $\alpha = \frac{R}{\ell}$ (the inverse Knudsen number). In the free molecular limit, $\alpha \to 0$, this mass flux is given by the well known Hertz-Knudsen formula which is reproduced in the next section. For a liquid droplet surrounded by a mixture of its vapor and an inert gas, the mass flux in the continuum limit is given by Maxwell's equation [3]. Only a few investigators have studied the problem in the intermediate regime. Brock [4] has considered the first correction term to the free molecular flux for a binary gas mixture, but replaced the Boltzmann equation with a linearized BGK model equation. Shankar [5] and also Sampson and Springer [6] approximate the distribution function by a two stream Maxwellian; the adjustable parameters in this function are then determined so that the distribution function will satisfy a limited number of moments of the Boltzmann equation. These approaches each involve approximations whose nature and magnitude are not clear and which therefore make it difficult to estimate the range of their

validity. It would thus appear to be useful to develop a more rigorous solution to the problem. The research reported here is an attempt in that direction.

We shall formulate a systematic expansion of the mass flux to a liquid droplet surrounded by its pure vapor in terms of the inverse Knudsen number α. This approach will be adequate in the nearly free molecular regime, where α is small compared to unity. This condition is encountered in many situations involving either homogeneous or heterogeneous nucleation, where the radius of the critical size clusters is indeed considerably smaller than the mean free path [7]. When the rate of change of mass of the droplet, Γ, is expanded around the free molecular limit ($\alpha \to 0$), we obtain

$$\Gamma = \Gamma^{(0)} + \Gamma^{(1)}\alpha + \tilde{\Gamma}^{(2)}\alpha^2 \ln\alpha + \ldots \qquad (1\text{-}1)$$

The successive coefficients of this series will be given by integrals associated with sequences of successive collisions among an increasing number of vapor molecules in the presence of the droplet. We shall in particular derive explicitly the collision integrals for the first three coefficients in the expansion (1-1).

The structure of the expansion (1-1) is analogous to the density expansion of the transport properties of gases [8]. In fact, we shall show that the collision integrals for the mass flux have a close similarity with the collision

integrals derived in earlier technical reports for the transport coefficients of a moderately dense gas [9,10]. A similarity of the same kind between the density expansion of the transport coefficients and the Knudsen number expansion for the drag coefficient of objects in rarefied gas flows was previously noted by Dorfman et al. [11,12].

In Section II we shall formulate the problem and specify the boundary conditions employed in the analysis. In Section III we shall derive a set of well-defined integrals that determine the coefficient $\Gamma^{(1)}$ of the first correction term. In the same section we develop a diagrammatic notation to represent sequences of collisions between the molecules. This notation will enable us to elucidate how the integrals of the expansion (1-1) for Γ are related to specific sequences of collisions among the molecules in the presence of the droplet. In Section IV we shall show that the next term is logarithmic in the Knudsen number and derive collision integrals for its coefficient $\tilde{\Gamma}^{(2)}$. In Section V we discuss the relationship between the new collision integrals and those derived earlier for transport coefficients and drag coefficients.

II. Steady State Mass Flux to and From a Liquid Drop

We shall calculate the net mass flux to a spherical liquid drop with radius R and temperature T_L surrounded by its pure vapor. The coordinate system is chosen so that the center of the droplet is located at the origin. The number density and temperature of the vapor at large distances from the droplet are maintained at n_∞ and T_∞, respectively.

We shall follow the previous authors [4,5,6] by considering the rate of change of the number of molecules in the droplet in the steady state approximation. That is, we assume that the droplet is sufficiently large so that we can neglect the change in the radius and temperature of the drop when a limited number of molecules condense onto or evaporate from it. Then the single-particle distribution function $F(\vec{r},\vec{v}_1)$ of the molecules in the vapor phase will satisfy the time-independent Boltzmann equation

$$\vec{v}_1 \cdot \frac{\partial F(\vec{r},\vec{v}_1)}{\partial \vec{r}} = \int d\vec{v}_2 \int d\hat{\sigma}_{12} k_{12} \left[F(\vec{r},\vec{v}_1') F(\vec{r},\vec{v}_2') - F(\vec{r},\vec{v}_1) F(\vec{r},\vec{v}_2) \right], \tag{2-1}$$

where $\vec{r}$ is a vector from the droplet center to some point in the vapor, $\hat{\sigma}_{12}$ the perihelion vector specifying the geometry of a collision between two molecules and $k_{12}(\vec{v}_{21},\hat{\sigma}_{12})$ a positive scalar factor, proportional to the differential

cross section for a collision, in the notation of Chapman and Cowling [13]. The velocities $\vec{v}_1', \vec{v}_2'$ are related to $\vec{v}_1, \vec{v}_2$ by:

$$\vec{v}_1' = \vec{v}_1 + (\vec{v}_{21} \cdot \hat{\sigma}_{12})\hat{\sigma}_{12},$$
$$\vec{v}_2' = \vec{v}_2 - (\vec{v}_{21} \cdot \hat{\sigma}_{12})\hat{\sigma}_{12}, \qquad (2\text{-}2)$$

where $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$.

We need to solve the Boltzmann equation, (2-1), subject to the appropriate boundary conditions both at the surface of the droplet and at infinity. Far from the droplet the pure vapor will be in equilibrium, so that:

$$\lim_{r \to \infty} F(\vec{r}, \vec{v}) = n_\infty \left(\frac{m}{2\pi k T_\infty} \right)^{\frac{3}{2}} \exp\left(- \frac{mv^2}{2kT_\infty} \right), \qquad (2\text{-}3)$$

where m is the mass of a vapor molecule and k is Boltzmann's constant.

We have already assumed that the liquid droplet is a sphere with radius R. To formulate the boundary conditions at the droplet surface, we must specify the mechanism for the interaction of the vapor and the liquid surface. This interaction is usually described in terms of a mass accommodation coefficient. For simplicity, we shall follow Shankar [5] and take this accommodation coefficient to be unity, i.e. all molecules that strike the surface will stick to it. All molecules that leave the surface shall

be assumed to be emitted diffusively with a Maxwellian distribution having the droplet temperature T_L and a number density n_L corresponding to the saturation pressure $P_v = n_L k T_L$ about a droplet of radius R. Thus the boundary condition on the distribution function at the droplet surface is:

$$F(\vec{R},\vec{v}) = n_L \left(\frac{m}{2\pi k T_L}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2kT_L}\right) \text{ for } \vec{v}\cdot\vec{R}>0. \qquad (2\text{-}4)$$

The pressure P_v, and thus n_L, is related to the saturation vapor pressure $P_{p.s.}$ for the vapor in equilibrium above a *planar* surface of its liquid at temperature T_L via the Thomson-Helmholtz equation [1].

We note that (2-4) represents the distribution function at the droplet surface of molecules in the vapor phase. Thus, strictly speaking, $F(\vec{R},\vec{v})$ is to be interpreted in this report as $\lim_{\delta\to 0} F(\vec{R}+\vec{\delta},\vec{v})$. With this in mind, the net mass flux Γ to the spherical droplet may be written in terms of the distribution function as:

$$\Gamma = -4\pi R^2 m \int d\vec{v}\ \vec{v}\cdot\hat{R}\ F(\vec{R},\vec{v}) \ , \qquad (2\text{-}5)$$

where $\hat{R} = \vec{R}/R$ is the unit vector in the direction of $\vec{R}$. The number of molecules in the droplet will increase or decrease depending on whether Γ is positive or negative. Since the net mass flux obviously vanishes when $n_L = n_\infty$ and $T_L = T_\infty$,

it becomes our task to evaluate Γ when $n_L \neq n_\infty$ and/or $T_L \neq T_\infty$.

The purpose of this report is to elucidate the structure of the collision integrals that determine the variation of Γ with the Knudsen number. The assumptions that the droplet has a spherical shape and that the mass accommodation coefficient is unity are not essential to our analysis, but are introduced for simplicity. The collision integrals to be derived can also be formulated for droplets of any geometry and the method can be generalized to the case where the mass accommodation coefficient is smaller than unity.

In order to exhibit the expansion parameter in the perturbation procedure, it is convenient to introduce dimensionless quantities [14]. For this purpose we define:

$$\vec{\rho} = \frac{\vec{r}}{R} \quad , \qquad \omega_\infty = \left(\frac{2kT_\infty}{m}\right)^{\frac{1}{2}} , \qquad \vec{\xi} = \frac{\vec{v}}{\omega_\infty} \quad ,$$

$$\kappa_{12} = \frac{k_{12}}{\pi\sigma^2\omega_\infty} \quad , \qquad f(\vec{\rho},\vec{\xi}) = \frac{\omega_\infty^3}{n_\infty} F(\vec{r},\vec{v}) \quad ,$$

$$n^* = \frac{n_L}{n_\infty} \quad , \qquad T^* = \frac{T_L}{T_\infty} \quad , \qquad (2\text{-}6)$$

where σ is a length parameter characterizing the range of the interaction potential between the molecules. The time-independent Boltzmann equation may then be written in dimensionless form:

$$\vec{\xi}_1 \cdot \frac{\partial f}{\partial \vec{\rho}}(\vec{\rho},\vec{\xi}_1) = \alpha \int d\vec{\xi}_2 \int d\hat{o}_{12} \kappa_{12} \left[f(\vec{\rho},\vec{\xi}_1') f(\vec{\rho},\vec{\xi}_2') - f(\vec{\rho},\vec{\xi}_1) f(\vec{\rho},\vec{\xi}_2) \right], \tag{2-7}$$

with $$\alpha \equiv \pi \sigma^2 R n_\infty . \tag{2-8}$$

The boundary conditions (2-3) and (2-4) become:

$$\lim_{\rho \to \infty} f(\vec{\rho},\vec{\xi}) = \pi^{-\frac{3}{2}} \exp(-\xi^2) \text{ for all } \xi, \tag{2-9a}$$

$$f(\hat{\rho},\vec{\xi}) = n^* (\pi T^*)^{-\frac{3}{2}} \exp\left(-\frac{\xi^2}{T^*}\right) \text{ for } \vec{\xi} \cdot \hat{\rho} > 0 . \tag{2-9b}$$

and the net mass flux Γ to the droplet is given by:

$$\Gamma = -4\pi R^2 m n_\infty \omega_\infty \int d\vec{\xi}\ \vec{\xi} \cdot \hat{\rho}\ f(\hat{\rho},\vec{\xi}) . \tag{2-10}$$

Since the mean free path ℓ of the vapor molecules is of the order $1/\pi\sigma^2 n_\infty$, the dimensionless parameter α in (2-7) is indeed the inverse Knudsen number R/ℓ. In this report we consider the nearly free molecular regime $\alpha << 1$ and solve the Boltzmann equation by a perturbation procedure in which we consider, successively, terms of higher order in α. Unfortunately, the name "Knudsen number iteration" is sometimes associated with a procedure in which one attempts to represent the solution of the Boltzmann equation by a *power* series in α [15]. Such a procedure leads to divergence difficulties which have the same physical origin as

the divergences encountered when the transport coefficients of a gas are represented by a power series in the density [8,16]. As already pointed out by Willis [17], it is not necessary in the perturbation procedure to impose the assumption that the solution be a power series in α. We shall follow a modified Knudsen number iteration procedure in which we collect terms that are of successively higher order in α, but do not prejudice the result by assuming that these terms are all powers of α.

The free molecular solution $f^{(0)}(\vec{\rho},\vec{\xi})$ is obtained in the limit $\alpha \to 0$, so that:

$$\vec{\xi} \cdot \frac{\partial f}{\partial \vec{\rho}}^{(0)}(\vec{\rho},\vec{\xi}) = 0 \ . \tag{2-11}$$

This equation, together with the boundary conditions (2-9), implies that $f^{(0)}(\vec{\rho},\vec{\xi})$ is a two-stream Maxwellian given by:

$$f^{(0)}(\vec{\rho},\vec{\xi}) = \begin{cases} \pi^{-\frac{3}{2}} \exp(-\xi^2) & \text{for } \vec{\xi} \in I(\rho) \\ n^*(\pi T^*)^{-\frac{3}{2}} \exp\left(-\dfrac{\xi^2}{T^*}\right) & \text{for } \vec{\xi} \in II(\rho) \end{cases} \tag{2-12}$$

For any $\vec{\rho}$, the regions $I(\rho)$ and $II(\rho)$ are velocity regions defined by:

$$\text{Region I} \qquad \begin{cases} \vec{\rho}\cdot\vec{\xi} < 0 \quad \text{or} \\ \vec{\rho}\cdot\vec{\xi} > 0 \ \textit{and} \ |\vec{\rho}\times\vec{\xi}|^2 - \xi^2 > 0 \ , \end{cases} \tag{2-13a}$$

Region II $\quad \vec{\rho}\cdot\vec{\xi}>0 \quad and \quad |\vec{\rho}\times\vec{\xi}|^2 - \xi^2 < 0 \ . \qquad (2\text{-}13b)$

For a given $\vec{\rho}$, the zeroth order term $f^{(0)}(\vec{\rho},\vec{\xi})$ is clearly discontinuous in velocity space. Region II is the free molecular cone of influence associated with the droplet as illustrated in Fig. 1; molecules having a velocity in this region have originated from the droplet and have arrived at the position $\vec{\rho}$ without suffering any collision. Molecules having a velocity in region I are unaffected by the presence of the droplet and may be considered as having arrived from infinity by free streaming.

As a short hand notation we shall write the two-stream Maxwellian (2-12) as:

$$f^{(0)}(\vec{\rho},\vec{\xi}) = f_I^{(0)}(\vec{\rho},\vec{\xi}) + f_{II}^{(0)}(\vec{\rho},\vec{\xi}) \quad , \qquad (2\text{-}14)$$

where $$f_I^{(0)}(\vec{\rho},\vec{\xi}) = \begin{cases} \pi^{-\frac{3}{2}} \exp(-\xi^2) = f_\infty(\xi) \text{ for } \vec{\xi} \in I(\rho) \\ 0 \text{ for } \vec{\xi} \in II(\rho) \ , \end{cases} \qquad (2\text{-}14a)$$

and $$f_{II}^{(0)}(\vec{\rho},\vec{\xi}) = \begin{cases} n^*(\pi T^*)^{-\frac{3}{2}} \exp(-\frac{\xi^2}{T^*}) \text{ for } \vec{\xi} \in II(\rho) \\ 0 \text{ for } \vec{\xi} \in I(\rho) \ . \end{cases} \qquad (2\text{-}14b)$$

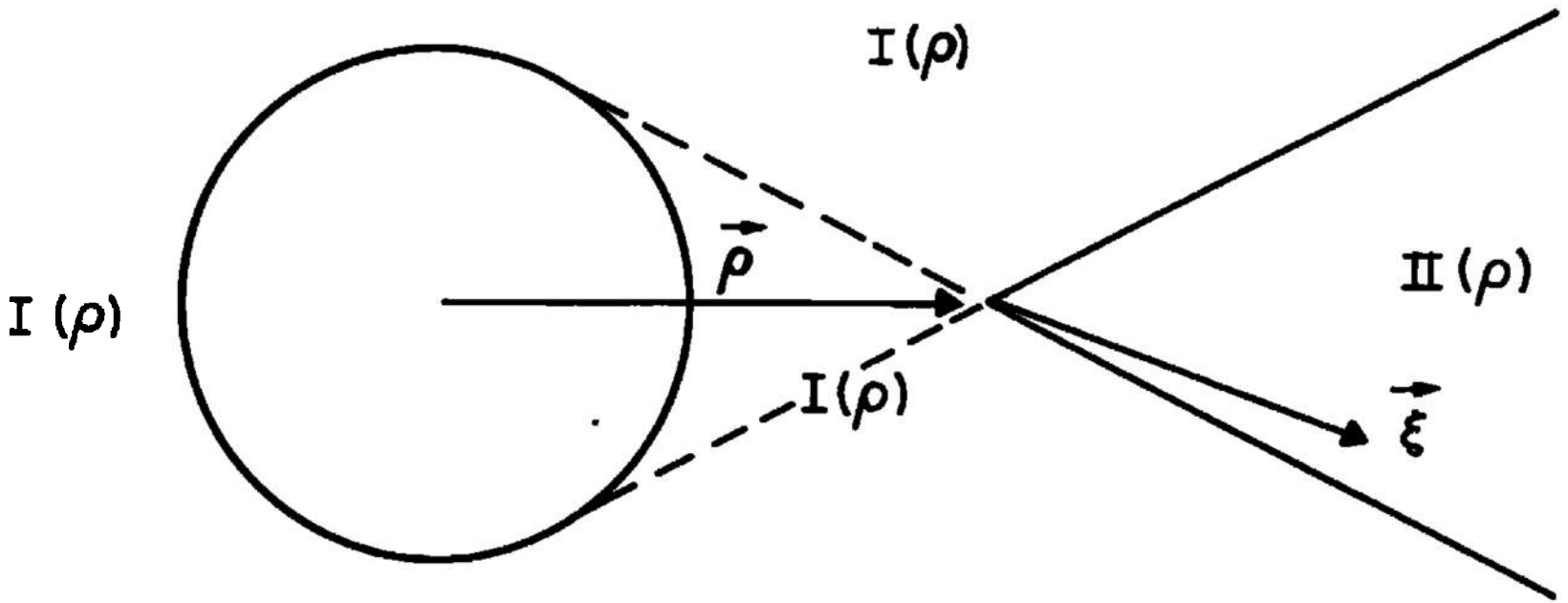

Fig. 1. The velocity regions I(ρ) and II(ρ) at a given position $\vec{\rho}$ in the vapor. Region II(ρ) is the free molecular cone of influence associated with the droplet.

The net mass flux Γ to the droplet in the free molecular approximation reduces to:

$$\Gamma^{(0)} = -4\pi R^2 m n_\infty \omega_\infty \int d\vec{\xi}\ \vec{\xi}\cdot\hat{\rho}\left[f_I^{(0)}(\hat{\rho},\vec{\xi}) + f_{II}^{(0)}(\hat{\rho},\vec{\xi})\right] =$$

$$= 4\pi R^2 m\left[n_\infty\left(\frac{kT_\infty}{2\pi m}\right)^{\frac{1}{2}} - n_L\left(\frac{kT_L}{2\pi m}\right)^{\frac{1}{2}}\right], \qquad (2\text{-}15)$$

which is the familiar Hertz-Knudsen formula [18].

III. First Correction Term to the Free Molecular Approximation

In order to obtain the first correction term $f^{(1)}(\vec{\rho},\vec{\xi})$ to the free molecular distribution function we approximate $f(\vec{\rho},\vec{\xi})$ in the right hand side of the Boltzmann equation (2-7) by the free molecular solution $f^{(0)}(\vec{\rho},\vec{\xi})$. We thus consider:

$$\vec{\xi}_1 \cdot \frac{\partial f^{(1)}(\vec{\rho},\vec{\xi}_1)}{\partial \vec{\rho}} =$$

$$= \alpha \int d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12} \left[f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(0)}(\vec{\rho},\vec{\xi}_2') - f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2) \right] . \tag{3-1}$$

Since the free molecular solution (2-12) satisfies the boundary conditions (2-9) exactly, we require that all higher order approximations $f^{(i)}(\vec{\rho},\vec{\xi})$ for $i > 0$ satisfy the boundary conditions:

$$\lim_{\rho \to \infty} f^{(i)}(\vec{\rho},\vec{\xi}) = 0 \quad \text{for all } \vec{\xi} , \tag{3-2a}$$

$$f^{(i)}(\hat{\rho},\vec{\xi}) = 0 \quad \text{for } \vec{\xi} \cdot \hat{\rho} > 0 . \tag{3-2b}$$

Equation (3-1) can be integrated to yield [14]:

$$f^{(1)}(\vec{\rho},\vec{\xi}_1) = f^{(1)}(\vec{\rho} - \vec{\xi}_1 t, \vec{\xi}_1) + \int_0^t d\tau J(\vec{\rho} - \vec{\xi}_1 \tau, \vec{\xi}_1) , \tag{3-3}$$

where $J(\vec{\rho},\vec{\xi})$ represents the right hand side of (3-1). In order to make use of the boundary conditions (3-2), we select the limit of the integration such that:

$$t = \begin{cases} \infty & \text{for } \vec{\xi}_1 \in I(\rho) \\ T(\vec{\rho},\vec{\xi}_1) & \text{for } \vec{\xi}_1 \in II(\rho) \end{cases} , \qquad (3\text{-}4)$$

where $$T(\vec{\rho},\vec{\xi}_1) = \frac{1}{|\vec{\xi}_1|}\left[\vec{\rho}\cdot\hat{\xi}_1 - \sqrt{(\vec{\rho}\cdot\hat{\xi}_1)^2 + 1 - \rho^2}\right] \qquad (3\text{-}5)$$

is the time it would take a molecule with velocity $\vec{\xi}_1 \in II(\rho)$ to travel from the droplet's surface to the position $\vec{\rho}$. This results in the vanishing of the integration constant in (3-3) for the problem under consideration. We thus obtain for the first correction term:

$$f^{(1)}(\vec{\rho},\vec{\xi}_1) = f_I^{(1)}(\vec{\rho},\vec{\xi}_1) + f_{II}^{(1)}(\vec{\rho},\vec{\xi}_1) , \qquad (3\text{-}6a)$$

with

$$f_I^{(1)}(\vec{\rho},\vec{\xi}_1) = \alpha\int_0^\infty d\tau_{12}\int d\vec{\xi}_2\int d\hat{\sigma}_{12}\kappa_{12}\Big[f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1')f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') +$$

$$- f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1)f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2)\Big] \text{ for } \vec{\xi}_1 \in I(\rho)$$

$$f_I^{(1)}(\vec{\rho},\vec{\xi}_1) = 0 \qquad \text{for } \vec{\xi}_1 \in II(\rho) ,$$

(3-6b)

and

$$f_{II}^{(1)}(\vec{\rho},\vec{\xi}_1) = \alpha \int_0^{T(\vec{\rho},\vec{\xi}_1)} d\tau_{12} \int d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12} \left[f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') + \right.$$

$$\left. - f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) \right] \text{ for } \vec{\xi}_1 \in II(\rho),$$

$$f_{II}^{(1)}(\vec{\rho},\vec{\xi}_1) = 0 \qquad \text{for } \vec{\xi}_1 \in I(\rho) \ . \tag{3-6c}$$

The τ_{12}-integration in these integrals extends over the free trajectory traversed by a molecule 1 with velocity $\vec{\xi}_1$.

If we substitute the expansion $f(\hat{\rho},\vec{\xi}) = f^{(0)}(\hat{\rho},\vec{\xi}) + f^{(1)}(\vec{\rho},\vec{\xi}) + \ldots$ into the expression (2-10) for the mass flux to the droplet, we obtain:

$$\Gamma = \Gamma^{(0)} + \alpha \Gamma^{(1)} + \ldots , \tag{3-7}$$

with

$$\Gamma^{(1)} = -4\pi R^2 m n_\infty \omega_\infty \alpha^{-1} \int d\vec{\xi}_1 \ \vec{\xi}_1 \cdot \hat{\rho} \ f^{(1)}(\hat{\rho},\vec{\xi}_1) =$$

$$= -4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\vec{\xi}_1 d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12} \ \vec{\xi}_1 \cdot \hat{\rho}$$

$$\cdot \left[f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') + \right.$$

$$\left. - f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) \right] . \tag{3-8}$$

The first correction term to $\Gamma^{(0)}$ is proportional to the inverse Knudsen number α provided, of course, that the integral (3-8) is convergent.

In this report, we assume that the interaction potential between a pair of vapor molecules has a finite range which is much smaller than R. It is then possible to decompose $\Gamma^{(1)}$ into a set of convergent integrals each of which is related to a particular sequence of successive collisions. For this purpose we use the relation $f_\infty(\xi_1')f_\infty(\xi_2') = f_\infty(\xi_1)f_\infty(\xi_2)$ for the distribution function at infinity and rewrite $\Gamma^{(1)}$ as:

$$\Gamma^{(1)} = -4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\vec{\xi}_1 d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12}\, \vec{\xi}_1\cdot\hat{\rho}$$

$$\cdot\left[f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1')f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') - f_\infty(\xi_1')f_\infty(\xi_2')\right] +$$

$$- 4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\vec{\xi}_1 d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12}\, \vec{\xi}_1\cdot\hat{\rho}$$

$$\cdot\left[f_\infty(\xi_1)f_\infty(\xi_2) - f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1)f^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2)\right]. \qquad (3\text{-}9)$$

As a next step we separate this integral into terms associated with the contributions $f_I^{(0)}$ and $f_{II}^{(0)}$ of the free

molecular flow solution $f^{(0)}$. For this purpose it is convenient to distinguish in f_∞ contributions from inside and outside the free molecular cone of influence. We therefore write:

$$f_\infty(\xi) = f_I^\infty(\vec{\rho},\vec{\xi}) + f_{II}^\infty(\vec{\rho},\vec{\xi}) \ , \tag{3-10}$$

where $$f_I^\infty(\vec{\rho},\vec{\xi}) = f_I^{(0)}(\vec{\rho},\vec{\xi}) \tag{3-10a}$$

and $$f_{II}^\infty(\vec{\rho},\vec{\xi}) = \begin{cases} 0 & \text{for } \vec{\xi} \in I(\rho) \\ \pi^{-\frac{3}{2}}\exp(-\xi^2) & \text{for } \vec{\xi} \in II(\rho) \end{cases} . \tag{3-10b}$$

The expression (3-9) for $\Gamma^{(1)}$ may then be divided into the four terms:

$$\Gamma^{(1)} = \Gamma^{(1)}_{II'I'} + \Gamma^{(1)}_{I'II'} + \Gamma^{(1)}_{II'II'} - \Gamma^{(1)}_{I\ II} \ , \tag{3-11}$$

with

$$\Gamma^{(1)}_{II'I'} = -4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\vec{\xi}_1 d\vec{\xi}_2 \int d\hat{\sigma}_{12} \kappa_{12}\ \vec{\xi}_1\cdot\hat{\rho} \tag{3-11a}$$

$$\cdot \left[f_{II}^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f_I^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') + \right.$$

$$\left. - f_{II}^\infty(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f_I^\infty(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') \right] ,$$

$$\Gamma^{(1)}_{I'II'} = -4\pi R^2 m_\infty \omega_\infty \int_0^\infty d\tau_{12} \int d\vec{\xi}_1 d\vec{\xi}_2 \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\hat{\sigma}_{12} \kappa_{12}\, \vec{\xi}_1\cdot\hat{\rho} \qquad (3\text{-}11b)$$

$$\cdot \left[f^{(0)}_I (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1') f^{(0)}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2') + \right.$$

$$\left. - f^{\infty}_I (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1') f^{\infty}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2') \right] ,$$

$$\Gamma^{(1)}_{II'II'} = -4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int d\vec{\xi}_1 d\vec{\xi}_2 \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\hat{\sigma}_{12} \kappa_{12}\, \vec{\xi}_1\cdot\hat{\rho} \qquad (3\text{-}11c)$$

$$\cdot \left[f^{(0)}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1') f^{(0)}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2') + \right.$$

$$\left. - f^{\infty}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1') f^{\infty}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2') \right] ,$$

$$\Gamma^{(1)}_{I\,II} = -4\pi R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int d\vec{\xi}_1 d\vec{\xi}_2 \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\hat{\sigma}_{12} \kappa_{12}\, \vec{\xi}_1\cdot\hat{\rho} \qquad (3\text{-}11d)$$

$$\cdot \left[f^{(0)}_I (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1) f^{(0)}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2) + \right.$$

$$\left. - f^{\infty}_I (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1) f^{\infty}_{II} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_2) \right] .$$

Note that the condition $\vec{\xi}_1\cdot\hat{\rho}<0$ implies that in (3-9):

$$f^{(0)} (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1) = f^{(0)}_I (\hat{\rho}-\vec{\xi}_1\tau_{12}, \vec{\xi}_1) \qquad (3\text{-}12)$$

for a droplet with a surface whose radius of curvature is positive everywhere. This has been used in obtaining (3-11d).

The condition $\vec{\xi}_1 \cdot \hat{\rho} < 0$ implies that molecule 1 is impinging upon the droplet with velocity $\vec{\xi}_1$. From (3-8) it is evident that the integral vanishes unless molecule 1 suffered a collision with molecule 2 at a time τ_{12} earlier. This collision is characterized by the perihelion vector $\hat{\delta}_{12}$. The velocities $\vec{\xi}_1$, $\vec{\xi}_2$ are the velocities *after* this collision and $\vec{\xi}_1'$, $\vec{\xi}_2'$ the velocities *prior* to this collision. The contribution to the integrand is dependent on whether, prior to this collision, molecule 1 and/or molecule 2 originated from the droplet or from infinity.

We thus consider the motion of two isolated molecules in the presence of the droplet. All of the possible collision sequences involving three or more successive collisions between two molecules and the droplet are schematically represented by the four diagrams of Fig. 2. The lines indicate the trajectories of the particles; the circle represents the droplet. The position of the molecules at time $\tau = 0$ is indicated by the dots; the velocities of molecules 1 and 2 at zero time are $\vec{\xi}_1$ and $\vec{\xi}_2$. At $\tau = 0$ molecule 1 is impinging upon the droplet, and in all diagrams the time is taken to increase when

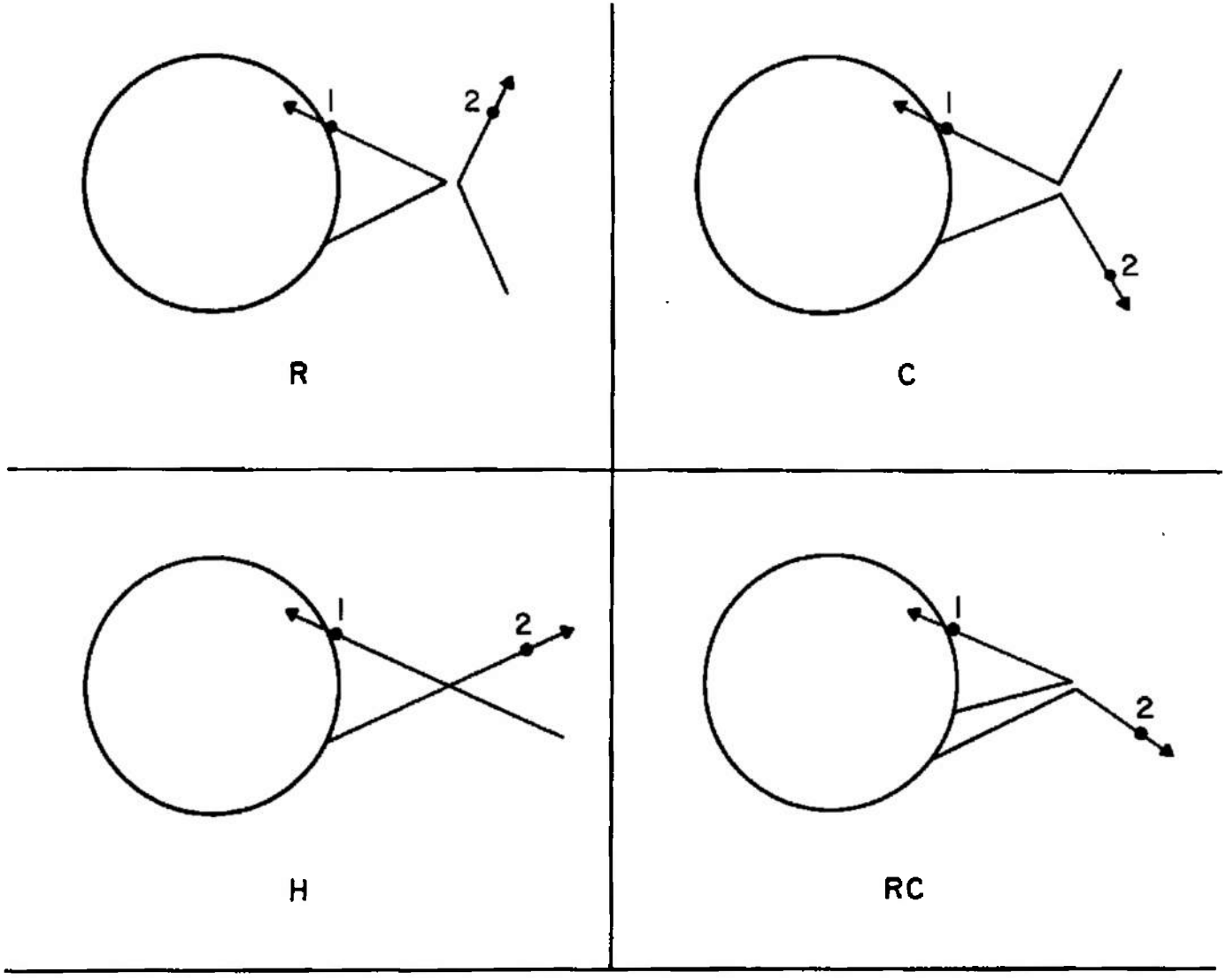

Fig. 2. The collision sequences among two vapor molecules and the droplet that are associated with the coefficient $\Gamma^{(1)}$ of the first inverse Knudsen number correction term. The lines represent the trajectories of molecules 1 and 2 and the circle represents the droplet.

the trajectories are traversed in the direction of the arrows. We also require, in all of the collisional sequences, that molecules 1 and 2 collide at time $\tau = -\tau_{12}$. The diagrams in Fig. 2 differ in the dynamical history of the molecules prior to the collision between 1 and 2. In the R- collision (recollision) we require that molecule 1 originate from the droplet, in the C- collision (cyclic collision) that molecule 2 originate from the droplet and in the RC- collision (recollision-cyclic) that *both* molecules 1 and 2 originate from the droplet. In the H- collision (hypothetical collision) we require that 2 originate from the droplet, but here we identify the velocities $\vec{\xi}_1'$, $\vec{\xi}_2'$ prior to the (12) collision with the velocities $\vec{\xi}_1$, $\vec{\xi}_2$ after the (12) collision. We shall refer to such a (12) collision as a non-interacting collision. In each of these collision sequences, we wish to remain non-committal about the possible occurrence of collisions that are not indicated explicitly. This interpretation of the diagrams is for convenience and has no effect on the exactness of our calculation. For instance, in the R- collision molecule 2 may or may not have originated from the droplet prior to the (12) collision and molecule 2 may or may not impinge upon the droplet after the (12) collision.

Each diagram in Fig. 2 determines a region of integration for the variables $\vec{\xi}_1$, $\vec{\xi}_2$, τ_{12}, $\hat{o}_{12}$ such that the collision sequence indicated takes place. From (3-11a) we see that the integrand of $\Gamma^{(1)}_{II'I'}$ vanishes unless particle 1 originated from the droplet and particle 2 from infinity. If we now replace the distribution functions by the appropriate Maxwellians and integrate over those regions of the variables $\vec{\xi}_1$, $\vec{\xi}_2$, τ_{12}, $\hat{o}_{12}$ associated with the recollision sequence of Fig. 2, we make an error since, in so doing, we have also implicitly included integration regions associated with the RC- collision. This contribution therefore needs to be subtracted. We thus obtain:

$$\Gamma^{(1)}_{II'I'} = -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(R)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$

$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\frac{\xi_1'^2}{T^*} + \xi_2'^2 \right) \right\} - \exp\left\{ -(\xi_1'^2 + \xi_2'^2) \right\} \right] +$$

$$+ 4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(RC)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$

$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\frac{\xi_1'^2}{T^*} + \xi_2'^2 \right) \right\} - \exp\left\{ -(\xi_1'^2 + \xi_2'^2) \right\} \right] . \tag{3-13}$$

The notation $\int_{(R)}$ indicates that the integration region is

limited so as to satisfy the conditions for a recollision to occur. The other collision integrals in (3-11) can be related to the diagrams of Fig. 2 in a similar way to yield:

$$\Gamma^{(1)}_{I'II'} = -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(C)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$
$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\xi_1'^2 + \frac{\xi_2'^2}{T^*} \right) \right\} - \exp\left\{ -(\xi_1'^2 + \xi_2'^2) \right\} \right] +$$
$$+ 4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(RC)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$
$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\xi_1'^2 + \frac{\xi_2'^2}{T^*} \right) \right\} - \exp\left\{ -(\xi_1'^2 + \xi_2'^2) \right\} \right], \tag{3-14}$$

$$\Gamma^{(1)}_{II'II'} = -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(RC)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$
$$\cdot \left[\frac{n^{*2}}{T^{*3}} \exp\left\{ -\left(\frac{\xi_1'^2}{T^*} + \frac{\xi_2'^2}{T^*} \right) \right\} - \exp\left\{ -(\xi_1'^2 + \xi_2'^2) \right\} \right], \tag{3-15}$$

$$\Gamma^{(1)}_{I\,II} = -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(H)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{o}_{12} \kappa_{12}\, \vec{\xi}_1 \cdot \hat{\rho}$$
$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\xi_1^2 + \frac{\xi_2^2}{T^*} \right) \right\} - \exp\left\{ -(\xi_1^2 + \xi_2^2) \right\} \right]. \tag{3-16}$$

Upon rearranging the terms in (3-13) through (3-16) we conclude that:

$$\Gamma^{(1)} = \Gamma_R^{(1)} + \Gamma_C^{(1)} + \Gamma_H^{(1)} + \Gamma_{RC}^{(1)} , \qquad (3\text{-}17)$$

where $\Gamma_R^{(1)}$, $\Gamma_C^{(1)}$, $\Gamma_H^{(1)}$ and $\Gamma_{RC}^{(1)}$ are given in Table I. The collision integrals $\Gamma_R^{(1)}$, $\Gamma_C^{(1)}$, $\Gamma_H^{(1)}$ are associated, respectively, with the R- C- and H- collision sequences which involve three successive collisions among two molecules and the droplet; $\Gamma_{RC}^{(1)}$ is related to the RC- collision sequence with four successive collisions. It is shown in Appendix A that these collision integrals are convergent, so that the coefficient $\Gamma^{(1)}$ of the term linear in α is finite.

TABLE 1 The collision integrals for the coefficient $\Gamma^{(1)}$ of the contribution proportional to a.

$$\Gamma^{(1)}_{R} \equiv -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(R)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \vec{\xi}_1 \cdot \hat{\rho} \left[\frac{n^*}{T^{*3/2}} \exp\left(-\left(\frac{\xi_1'^2}{T^*} + \xi_2'^2\right)\right) - \exp\left(-\left(\xi_1'^2 + \xi_2'^2\right)\right) \right]$$

$$\Gamma^{(1)}_{C} \equiv -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(C)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \vec{\xi}_1 \cdot \hat{\rho} \left[\frac{n^*}{T^{*3/2}} \exp\left(-\left(\xi_1'^2 + \frac{\xi_2'^2}{T^*}\right)\right) - \exp\left(-\left(\xi_1'^2 + \xi_2'^2\right)\right) \right]$$

$$\Gamma^{(1)}_{H} \equiv +4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(H)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \vec{\xi}_1 \cdot \hat{\rho} \left[\frac{n^*}{T^{*3/2}} \exp\left(-\left(\xi_1^2 + \frac{\xi_2^2}{T^*}\right)\right) - \exp\left(-\left(\xi_1^2 + \xi_2^2\right)\right) \right]$$

$$\Gamma^{(1)}_{RC} \equiv -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_{(RC)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \vec{\xi}_1 \cdot \hat{\rho} \left[\frac{n^{*2}}{T^{*3}} \exp\left(-\left(\frac{\xi_1'^2}{T^*} + \frac{\xi_2'^2}{T^*}\right)\right) + \exp\left(-\left(\xi_1'^2 + \xi_2'^2\right)\right) \right.$$

$$\left. - \frac{n^*}{T^{*3/2}} \exp\left(-\left(\frac{\xi_1'^2}{T^*} + \xi_2'^2\right)\right) - \frac{n^*}{T^{*3/2}} \exp\left(-\left(\xi_1'^2 + \frac{\xi_2'^2}{T^*}\right)\right) \right]$$

IV. Second Correction Term to the Free Molecular Approximation

We consider the solutions $f^{(0)}(\vec{\rho},\vec{\xi})$ and $f^{(1)}(\vec{\rho},\vec{\xi})$ as the first two terms of an expansion for the distribution function:

$$f(\vec{\rho},\vec{\xi}) = f^{(0)}(\vec{\rho},\vec{\xi}) + f^{(1)}(\vec{\rho},\vec{\xi}) + f^{(2)}(\vec{\rho},\vec{\xi}) + \ldots \quad (4\text{-}1)$$

If we substitute this expansion into the Boltzmann equation (2-7) and neglect terms which are obviously of higher order, we obtain the equation:

$$\vec{\xi}_1 \cdot \frac{\partial f^{(2)}}{\partial \vec{\rho}}(\vec{\rho},\vec{\xi}_1) = \alpha \int d\vec{\xi}_2 d\delta_{12} \kappa_{12}$$

$$\cdot \left\{ \left[f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(1)}(\vec{\rho},\vec{\xi}_2') + f^{(1)}(\vec{\rho},\vec{\xi}_1') f^{(0)}(\vec{\rho},\vec{\xi}_2') + \right.\right.$$

$$\left. - f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(1)}(\vec{\rho},\vec{\xi}_2) - f^{(1)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2) \right] +$$

$$+ \left[f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(2)}(\vec{\rho},\vec{\xi}_2') + f^{(2)}(\vec{\rho},\vec{\xi}_1') f^{(2)}(\vec{\rho},\vec{\xi}_2') + \right.$$

$$\left. - f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(2)}(\vec{\rho},\vec{\xi}_2) - f^{(2)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2) \right] +$$

$$\left. + \left[f^{(1)}(\vec{\rho},\vec{\xi}_1') f^{(1)}(\vec{\rho},\vec{\xi}_2') - f^{(1)}(\vec{\rho},\vec{\xi}_1) f^{(1)}(\vec{\rho},\vec{\xi}_2) \right] \right\} . \quad (4\text{-}2)$$

In the previous section we showed that $f^{(1)}$ leads to a correction term linear in the expansion parameter α. If

we now were to assume that $f^{(2)}$ is proportional to α^2, we would retain only the terms involving $f^{(0)}f^{(1)}$ on the right hand side of (4-2). This equation, thus truncated, would yield in analogy to (3-6):

$$f^{(2)}(\vec{\rho},\vec{\xi}_1) = \alpha \int_0^t d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12}$$

$$\cdot \Big[f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') +$$

$$+ f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') +$$

$$- f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) +$$

$$- f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) \Big] , \qquad (4\text{-}3)$$

where the upper limit t of the τ_{12}- integration is again given by (3-4). The resulting contribution to the flux Γ would then read:

$$\Gamma = \Gamma^{(0)} + \alpha\Gamma^{(1)} + \alpha^2\Gamma^{(2)} + \ldots \qquad (4\text{-}4)$$

with

$$\Gamma^{(2)} = -4\pi R^2 m n_\infty \omega_\infty \alpha^{-1} \int_{\vec{\xi}_1 \cdot \hat{\rho} < 0} d\vec{\xi}_1 \vec{\xi}_1 \cdot \hat{\rho} \int_0^\infty d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12}$$

$$\cdot \Big[f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1') f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2') +$$

$$+ f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1') f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2') +$$

$$- f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2) +$$

$$- f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2) \Big] . \qquad (4\text{-}5)$$

In the previous section we showed that $\Gamma^{(1)}$ is determined by integrals associated with three or more successive collisions among two molecules and the droplet. The expression (4-5) can similarly be analyzed in a manner that will be discussed later in this section. It turns out that (4-5) can be decomposed into a set of integrals associated with four or more successive collisions among three molecules and the droplet. The leading terms are determined by the integrals corresponding to the sequences of four collisions depicted in Fig. 3. However, as shown in Appendix A, the phase space associated with these events behaves as τ_{12}^{-1} for large values of τ_{12} and thus the integrals diverge logarithmically. Our original assumption, therefore, that $f^{(2)}$ yields a contribution proportional to

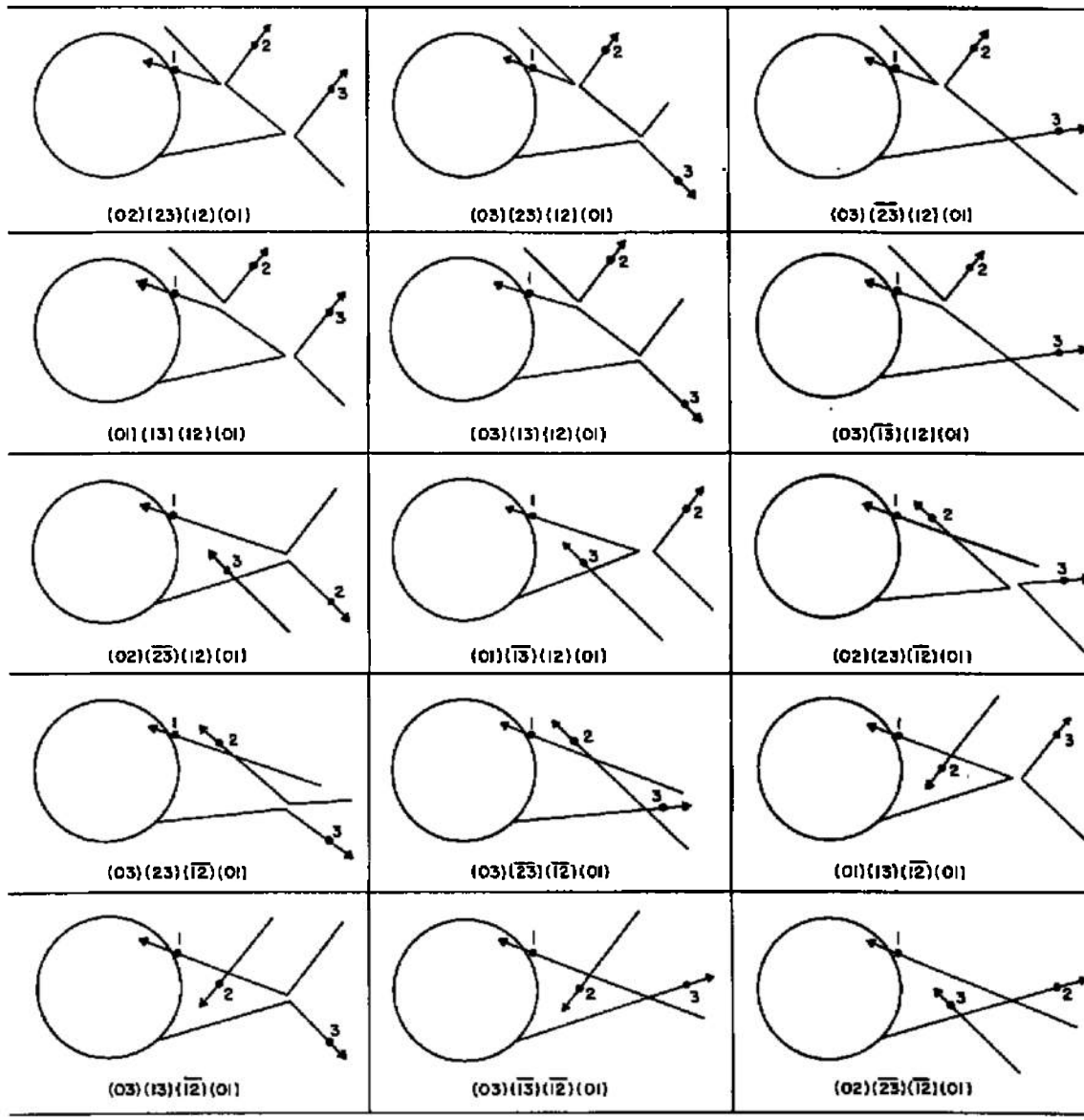

Fig. 3. The collision sequences among three vapor molecules and the droplet. They are associated with $\Gamma^{(2)}$ in (4-5) and with the coefficient $\tilde{\Gamma}^{(2)}$ of the correction term proportional to $\alpha^2 \ln\alpha$.

α^2, is not justified and we need to consider the full equation (4-2).

Since, on the right hand side of (4-2), the Boltzmann collision operator operates on the unknown function $f^{(2)}$, solving this equation poses a formidable task. It is, however, possible to extract the contribution to the mass flux which is of lowest order in α. For this purpose, it suffices to retain on the right side of (4-2) the expressions involving $f^{(0)}f^{(1)}$ and the term which is directly proportional to $f^{(2)}(\vec{\rho},\vec{\xi}_1)$:

$$\alpha \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} f^{(2)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2) \quad . \tag{4-6}$$

We thus consider the equation:

$$\vec{\xi}_1 \cdot \frac{\partial f^{(2)}(\vec{\rho},\vec{\xi}_1)}{\partial \vec{\rho}} + \alpha \nu(\xi_1) f^{(2)}(\vec{\rho},\vec{\xi}_1) =$$

$$= \alpha \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \left[f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(1)}(\vec{\rho},\vec{\xi}_2') + f^{(1)}(\vec{\rho},\vec{\xi}_1') f^{(0)}(\vec{\rho},\vec{\xi}_2') + \right.$$

$$\left. - f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(1)}(\vec{\rho},\vec{\xi}_2) - f^{(1)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2) \right], \tag{4-7}$$

where $\nu(\xi_1)$ is the collision frequency:

$$\nu(\xi_1) \equiv \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} f_\infty(\xi_2) \quad . \tag{4-8}$$

In writing (4-8) we have approximated $f^{(0)}(\vec{\rho},\vec{\xi}_2)$ in (4-6) by the Maxwell distribution $f_\infty(\xi_2)$. The justification for this will be explained shortly.

The simplified equation (4-7) can be readily integrated to yield:

$$\begin{aligned} f^{(2)}(\vec{\rho},\vec{\xi}_1) = \alpha \int_0^t d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} e^{-\alpha\nu\tau_{12}} \\ \cdot \Big[f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') + \\ + f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1') f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2') + \\ - f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) + \\ - f^{(1)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_1) f^{(0)}(\vec{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_2) \Big] \quad . \end{aligned} \tag{4-9}$$

This result is the same as (4-3) except for the inclusion of the exponential factor $e^{-\alpha\nu\tau_{12}}$. This damping factor will insure that the resulting collision integrals are convergent.

With this damping factor introduced into (4-5), we conclude that for large values of τ_{12} the leading term in the second correction to the mass flux Γ will vary as:

$$\alpha^2 \int d\tau_{12} e^{-\alpha\nu\tau_{12}} \frac{A}{\tau_{12}} = A\alpha^2 \ln\alpha + \text{terms of higher order in } \alpha. \tag{4-10}$$

The situation thus appears to be quite analogous to the exponential damping of the collision integrals in the theory of the density dependence for the transport coefficients of a gas [19,20]. While the expression (4-9) for $f^{(2)}$ does not represent a complete solution of the original equation (4-2), it does contain all necessary information to determine the coefficient of the contribution to the mass flux proportional to $\alpha^2 \ln\alpha$. The reason for this is twofold. First, the terms containing $f^{(1)} f^{(1)}$ give a contribution to Γ which is of order α^3. Secondly, the neglected terms in (4-2) involving $f^{(2)}$ and also the replacement of $f^{(0)}(\vec{\rho}, \vec{\xi}_2)$ in (4-6) by $f_\infty(\xi_2)$ modify the details of the exponential damping factor, but do not change the coefficient A in (4-10). The mathematical analysis to substantiate these assertions is quite complex and is, to the extent feasible, presented in Appendix B. In the main body of this report we shall concentrate on formulating the collision integrals that will enable us to calculate the coefficient of the contribution proportional to $\alpha^2 \ln\alpha$.

We thus consider:

$$\Gamma = \Gamma^{(0)} + \Gamma^{(1)}\alpha + \tilde{\Gamma}^{(2)}\alpha^2 \ln\alpha + \ldots \tag{4-11}$$

where:

$$\tilde{\Gamma}^{(2)} = -4\pi R^2 m n_\infty \omega_\infty \lim_{\alpha \to 0} \frac{1}{\alpha \ln \alpha} \int_{\vec{\xi}_1 \cdot \hat{\rho} < 0} d\vec{\xi}_1 \vec{\xi}_1 \cdot \hat{\rho} \int_0^\infty d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} e^{-\alpha \nu \tau_{12}}$$

$$\cdot \left[f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1') f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2') + \right.$$

$$+ f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1') f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2') +$$

$$- f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2) +$$

$$\left. - f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_2) \right] . \qquad (4\text{-}12)$$

is obtained by substituting (4-9) into (2-10). This result differs from (4-5) due to the inclusion of the exponential damping factor.

In order to avoid the repetition of unnecessary details, we introduce a shorthand notation:

$$\left[f^{(0)}(i) f^{(1)}(j) \right] \equiv -4\pi R^2 m n_\infty \omega_\infty \lim_{\alpha \to 0} \frac{1}{\alpha \ln \alpha} \int_{\vec{\xi}_1 \cdot \hat{\rho} < 0} d\vec{\xi}_1 \vec{\xi}_1 \cdot \hat{\rho} \int_0^\infty d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12}$$

$$\cdot \kappa_{12} e^{-\alpha \nu \tau_{12}} f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_i) f^{(1)}(\hat{\rho} - \xi_1 \tau_{12}, \vec{\xi}_j) , \qquad (4\text{-}13)$$

so that

$$\tilde{\Gamma}^{(2)} = \left[f^{(0)}(1') f^{(1)}(2') \right] + \left[f^{(1)}(1') f^{(0)}(2') \right] +$$

$$- \left[f^{(0)}(1) f^{(1)}(2) \right] - \left[f^{(1)}(1) f^{(0)}(2) \right] , \qquad (4\text{-}14)$$

where all distribution functions in the integrands are to be evaluated at the position $\vec{\rho} = \hat{\rho} - \vec{\xi}_1 \tau_{12}$.

We shall demonstrate that this coefficient $\tilde{\Gamma}^{(2)}$ is determined by a set of integrals associated with sequences of collisions among three molecules and the droplet. For this purpose we first write, in accordance with (2-14) and (3-6a) $f^{(0)} = f_I^{(0)} + f_{II}^{(0)}$ and $f^{(1)} = f_I^{(1)} + f_{II}^{(1)}$ to obtain:

$$\begin{aligned}
\tilde{\Gamma}^{(2)} = & \left[f_I^{(0)}(1')f_I^{(1)}(2')\right] + \left[f_I^{(1)}(1')f_I^{(0)}(2')\right] + \\
& + \left[f_I^{(0)}(1')f_{II}^{(1)}(2')\right] + \left[f_I^{(1)}(1')f_{II}^{(0)}(2')\right] + \\
& + \left[f_{II}^{(0)}(1')f_I^{(1)}(2')\right] + \left[f_{II}^{(1)}(1')f_I^{(0)}(2')\right] + \\
& + \left[f_{II}^{(0)}(1')f_{II}^{(1)}(2')\right] + \left[f_{II}^{(1)}(1')f_{II}^{(0)}(2')\right] + \\
& - \left[f_I^{(0)}(1)\, f_I^{(1)}(2)\right] + \left[f_I^{(1)}(1)\, f_I^{(0)}(2)\right] + \\
& - \left[f_I^{(0)}(1)\, f_{II}^{(1)}(2)\right] - \left[f_I^{(1)}(1)\, f_{II}^{(0)}(2)\right] .
\end{aligned} \tag{4-15}$$

Here we have used the fact that in the integrand of (4-12) $\vec{\xi}_1 \in I(|\hat{\rho} - \vec{\xi}_1 \tau_{12}|)$ so that $f^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) = f_I^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1)$ and $f^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1) = f_I^{(1)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1)$.

As a second step we decompose $f_I^{(1)}$, given by (3-6b) in the same manner as was done in (3-11) for $\Gamma^{(1)}$. We then obtain:

$$f_I^{(1)}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i) \equiv f^{(1)}_{I,II'I'}(i) + f^{(1)}_{I,I'II'}(i) +$$

$$+ f^{(1)}_{I,II'II'}(i) - f^{(1)}_{I,I\ II}(i) , \qquad (4\text{-}16)$$

where we have, for $\vec{\xi}_i \in I(|\hat{\rho}-\vec{\xi}_1\tau_{12}|)$:

$$f^{(1)}_{I,II'I'}(i) \equiv \alpha \int_0^\infty d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f_{II}^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_I^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f_{II}^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_I^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right] , \qquad (4\text{-}16a)$$

$$f^{(1)}_{I,I'II'}(i) = \alpha \int_0^\infty d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f_I^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_{II}^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f_I^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_{II}^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right] , \qquad (4\text{-}16b)$$

$$f^{(1)}_{I,II'II'}(i) = \alpha \int_0^\infty d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f_{II}^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_{II}^{(0)}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f_{II}^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f_{II}^{\infty}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right] , \qquad (4\text{-}16c)$$

$$f^{(1)}_{I,\,I\ II}(i) \equiv \alpha \int_0^\infty d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) + \right.$$

$$\left. - f^{\infty}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) \right] . \qquad (4\text{-}16d)$$

For $\vec{\xi}_i \in II(|\hat{\rho}-\vec{\xi}_1\tau_{12}|)$ we take, just as in (3-6b):

$$f^{(1)}_{I,II'I'}(i) = f^{(1)}_{I,I'II'}(i) = f^{(1)}_{I,II'II'}(i) = f^{(1)}_{I,\,I\ II}(i) = 0. \qquad (4\text{-}16e)$$

In (4-16a) through (4-16d), $\hat{\sigma}_{i3}$ is the perihelion vector of a collision between molecules i and 3 taking place at the position $\vec{\rho} = \hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3}$. The initial velocities prior to this collision are $\vec{\xi}_i''$ and $\vec{\xi}_3''$ and the final velocities after this collision are $\vec{\xi}_i$ and $\vec{\xi}_3$.

Similarly the function $f^{(1)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)$, given by (3-6c), is decomposed as:

$$f^{(1)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i) = f^{(1)}_{II,II'I'}(i) + f^{(1)}_{II,I'II'}(i) +$$

$$+ f^{(1)}_{II,II'II'}(i) - f^{(1)}_{II,II\ I}(i) - f^{(1)}_{II,II\ II}(i) , \qquad (4\text{-}17)$$

where for $\vec{\xi}_i \in II(|\hat{\rho}-\vec{\xi}_1\tau_{12}|)$

$$f^{(1)}_{II,II'I'}(i) = \alpha \int_0^{T(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)} d\tau_{i3} \int d\vec{\xi}_3 d\hat{o}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{(0)}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{\infty}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right], \quad (4\text{-}17a)$$

$$f^{(1)}_{II,I'II'}(i) = \alpha \int_0^{T(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)} d\tau_{i3} \int d\vec{\xi}_3 d\hat{o}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f^{\infty}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right]; \quad (4\text{-}17b)$$

$$f^{(1)}_{II,II'II'}(i) = \alpha \int_0^{T(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)} d\tau_{i3} \int d\vec{\xi}_3 d\hat{o}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') + \right.$$

$$\left. - f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i'') f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3'') \right], \quad (4\text{-}17c)$$

$$f^{(1)}_{II,II\ I}(i) = \alpha \int_0^{T(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)} d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{(0)}_{I}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) + \right.$$

$$\left. - f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{\infty}_{I}(\hat{\rho}-\vec{\xi}_i\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) \right], \qquad (4\text{-}17d)$$

$$f^{(1)}_{II,II\ II}(i) = \alpha \int_0^{T(\hat{\rho}-\vec{\xi}_1\tau_{12},\vec{\xi}_i)} d\tau_{i3} \int d\vec{\xi}_3 d\hat{\sigma}_{i3} \kappa_{i3}$$

$$\cdot \left[f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{(0)}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) + \right.$$

$$\left. - f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_i) f^{\infty}_{II}(\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_i\tau_{i3},\vec{\xi}_3) \right]. \qquad (4\text{-}17e)$$

Just as in (3-6c), it is again understood that for $\vec{\xi}_i \in I(|\hat{\rho}-\vec{\xi}_1\tau_{12}|)$

$$f^{(1)}_{II,II'I'}(i) = f^{(1)}_{II,I'II'}(i) = f^{(1)}_{II,II'II'}(i) =$$

$$= f^{(1)}_{II,II\ I}(i) = f^{(1)}_{II,II\ II}(i) = 0.$$

In order to investigate the structure of the collision integrals determining $\tilde{\Gamma}^{(2)}$, we consider as an example the term:

$$\left[f_I^{(0)}(1') f_{I,II'I'}^{(1)}(2') \right] = -4\pi R^2 m n_\infty \omega_\infty \lim_{\alpha \to 0} \frac{1}{\ln \alpha}$$

$$\cdot \int_{\vec{\xi}_1 \cdot \hat{\rho} < 0} d\vec{\xi}_1 \vec{\xi}_1 \cdot \hat{\rho} \int_0^\infty d\tau_{12} \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} e^{-\alpha \nu \tau_{12}} \int_0^\infty d\tau_{2'3} \int d\vec{\xi}_3 d\hat{\sigma}_{2'3} \kappa_{2'3}$$

$$\cdot f_I^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12}, \vec{\xi}_1') \left[f_{II}^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12} - \vec{\xi}_2' \tau_{2'3}, \vec{\xi}_2'') f_I^{(0)}(\hat{\rho} - \vec{\xi}_1 \tau_{12} - \vec{\xi}_2' \tau_{2'3}, \vec{\xi}_3'') - \right.$$

$$\left. - f_{II}^{\infty}(\hat{\rho} - \vec{\xi}_1 \tau_{12} - \vec{\xi}_2' \tau_{2'3}, \vec{\xi}_2'') f_I^{\infty}(\hat{\rho} - \vec{\xi}_1 \tau_{12} - \vec{\xi}_2' \tau_{2'3}, \vec{\xi}_3'') \right] , \qquad (4\text{-}18)$$

which is obtained when (4-16a) is substituted into the first term of (4-15). The integrand in (4-18) corresponds to those phases of molecule 1, 2 and 3 such that:

(a) at $\vec{\rho} = \hat{\rho}$, corresponding to the time $\tau = 0$, molecule 1 is impinging upon the droplet;

(b) at $\vec{\rho} = \hat{\rho} - \vec{\xi}_1 \tau_{12}$, corresponding to the time $\tau = -\tau_{12}$, molecule 1 collides with molecule 2; (the velocities of these molecules *prior* to this collision are $\vec{\xi}_1'$ and $\vec{\xi}_2'$ and *after* this collision $\vec{\xi}_1$ and $\vec{\xi}_2$);

(c) at $\vec{\rho} = \hat{\rho} - \vec{\xi}_1 \tau_{12} - \vec{\xi}_2' \tau_{2'3}$, corresponding to the time $\tau = -(\tau_{12} + \tau_{2'3})$, molecule 2 collides with molecule 3. The velocities of these molecules *prior* to the collision are $\vec{\xi}_2''$ and $\vec{\xi}_3''$ and *after* the collision are $\vec{\xi}_2'$ and $\vec{\xi}_3$;

(d) before the collision between molecules 2 and 3, the velocity of 2 must be within region II, which means that molecule 2 originated from the droplet.

This collision sequence is shown schematically in Fig. 4 using the diagrammatic notation developed in the previous section. The integral (4-18) represents an integral over all phase points of molecules 1, 2 and 3 which allow for the occurrence of the sequence depicted in this diagram.

In the previous section we referred to the collision sequences that contributed to the first coefficient $\Gamma^{(1)}$ as R-, C-, H- and RC- collisions. In order to specify the collision integrals for the coefficient $\tilde{\Gamma}^{(2)}$ we need a more systematic notation. We shall indicate an interacting collision between molecules i and j by (ij) and a non-interacting collision between i and j by $(\overline{ij})$. A collision between molecule k and the droplet will be denoted by (Ok) where O refers to the droplet. A collision sequence is represent by a left-to-right juxtaposition of these symbols. In this notation the R-, C- and H- collisions introduced in the previous section can be represented by (01)(12)(01), (02)(12)(01) and (02)$(\overline{12})$(01), respectively, and the diagram of Fig. 4 by (02)(23)(12)(01). Thus the contribution (4-18) to $\tilde{\Gamma}^{(2)}$ becomes:

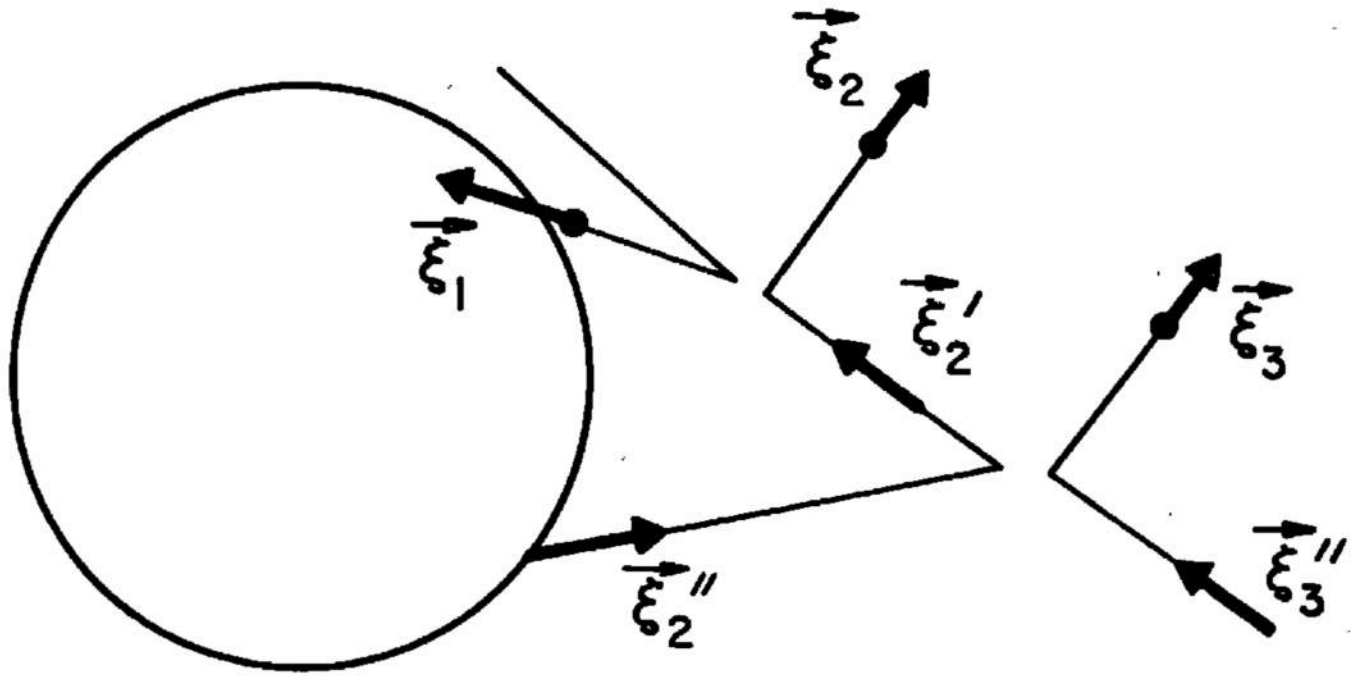

Fig. 4. Example of a sequence of four collisions among three vapor molecules and the droplet. In this example molecule 2, which has originated from the droplet, first collides with 3 and subsequently with 1 in such a manner that molecule 1 will impinge upon the droplet.

$$\tilde{\Gamma}^{(2)}_{(02)(23)(12)(01)} \equiv \left[f_I^{(0)}(1') f^{(1)}_{I,II'I'}(2') \right] =$$

$$= -4\pi R^2 m n_\infty \omega_\infty \lim_{\alpha \to 0} \frac{1}{\ln \alpha} \int_{(02)(23)(12)(01)} d\vec{\xi}_1 d\tau_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} d\tau_{2'3} d\vec{\xi}_3 d\hat{\sigma}_{2'3}$$

$$\cdot \kappa_{12} \kappa_{2'3} \vec{\xi}_1 \cdot \hat{\rho} e^{-\alpha \nu \tau_{12}} \pi^{-\frac{3}{2}} \exp\{-\xi_1''^2\} \left[n^* \pi^{-3} T^{*-\frac{3}{2}} \exp\{-(\frac{\xi_2''^2}{T^*} + \xi_3''^2)\} + \right.$$

$$\left. - \pi^{-3} \exp\{-(\xi_2''^2 + \xi_3''^2)\} \right] , \qquad (4\text{-}19)$$

where the symbol $\int_{(02)(23)(12)(01)}$ means that the integration extends over all phases of molecules 1, 2 and 3 corresponding to the collision sequence (02)(23)(12)(01).

If we substitute (4-16) and (4-17) into (4-15) we find that $\tilde{\Gamma}^{(2)}$ appears to be a sum of fifty-three terms each of which may be associated with a sequence of collisions among three vapor molecules and the droplet. However, many of these terms correspond to sequences that involve more than four successive collisions. As an illustration we examine the two terms $[f^{(1)}_{I,II'II'}(1') f_I^{(0)}(2')]$ and $[f^{(1)}_{II,II'I'}(1') f_I^{(0)}(2')]$ which correspond to the collision sequences shown in Fig. 5. These two terms both require a sequence of collisions which in our notation can be indicated by (01)(13)(12)(01). The term $[f_{I,II'II'}(1') f_I^{(0)}(2')]$

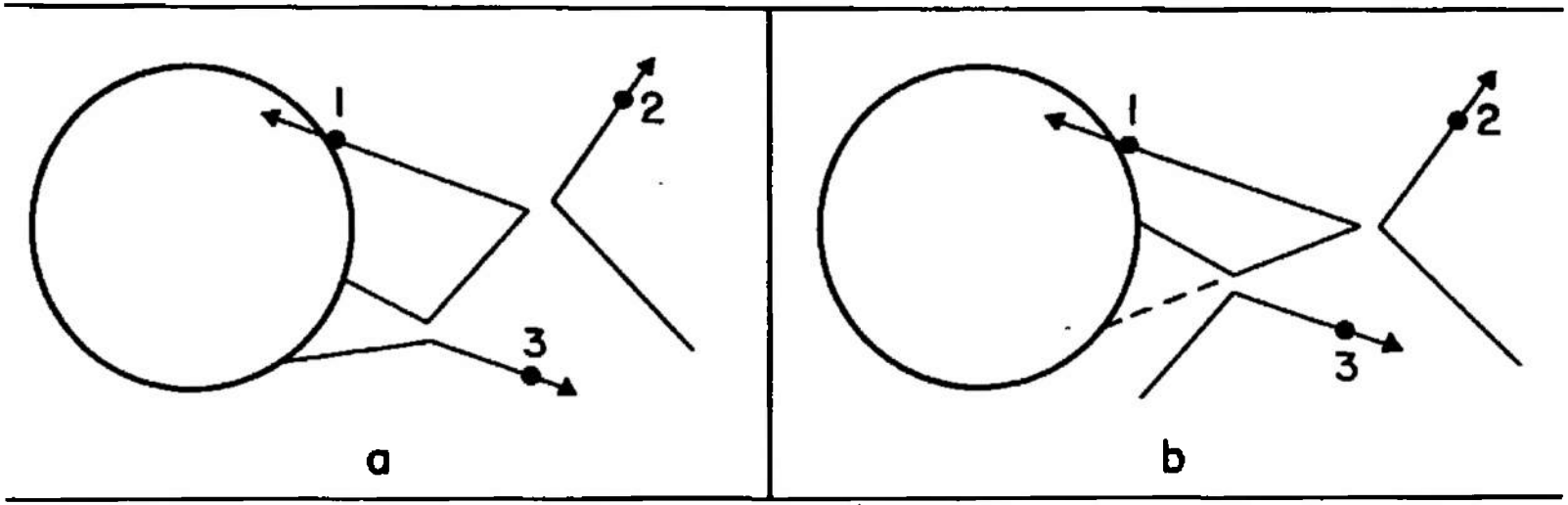

Fig. 5. Examples of sequences of five collisions among three vapor molecules and the droplet.

(a) Diagram corresponding to $[f^{(1)}_{I,II'II'}(1')f^{(0)}_{I}(2')]$,

(b) Diagram corresponding to $[f^{(1)}_{II,II'I'}(1')f^{(0)}_{I}(2')]$.

requires, in addition, that $\vec{\xi}_3'' \in II(|\hat{\rho}-\vec{\xi}_1\tau_{12}-\vec{\xi}_1'\tau_{1'3}|)$ which means that not only 1, but also 3 must have originated initially from the droplet. The term $[f^{(1)}_{II,II'I'}(1')f^{(0)}_{I}(2')]$ does not involve the latter condition, but requires instead $\vec{\xi}_1' \in II(|\hat{\rho}-\vec{\xi}_1\tau_{12}|)$ this constraint implies that the phase of molecule 1 must be such that it also would have originated from the droplet if we ignore the velocity change caused by the (13) collision. Both terms therefore involve constraints related to five collisions. In fact, it can be readily verified that terms in $\tilde{\Gamma}^{(2)}$ which contain either $f^{(0)}_{II}$ and/or any of the following: $f^{(1)}_{I,II'II''}$, $f^{(1)}_{I,II'I''}$, $f^{(1)}_{II,I'II''}$, $f^{(1)}_{II,II'II''}$, $f^{(1)}_{II,II\ II'}$ all correspond to sequences of five or more collisions among three molecules and the droplet. However as discussed in Appendix A such terms lead to integrals of the form:

$$\lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int d\tau_{12} e^{-\alpha\nu\tau_{12}} \frac{1}{\tau_{12}^{2+\gamma}} = 0 \ , \qquad (4\text{-}20)$$

with $\gamma \geq 0$ and, therefore, do not yield a contribution to $\tilde{\Gamma}^{(2)}$. In order to determine the coefficient of the $\alpha^2\ln\alpha$ term it is sufficient to retain only the collision integrals related to four successive collisions. We thus obtain:

$$\tilde{\Gamma}^{(2)} = \tilde{\Gamma}^{(2)}_{(02)\,(23)\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(23)\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(\overline{23})\,(12)\,(01)} +$$

$$+\tilde{\Gamma}^{(2)}_{(01)\,(13)\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(13)\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(\overline{13})\,(12)\,(01)} +$$

$$+\tilde{\Gamma}^{(2)}_{(02)\,(\overline{23})\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(01)\,(\overline{13})\,(12)\,(01)} + \tilde{\Gamma}^{(2)}_{(02)\,(23)\,(\overline{12})\,(01)} +$$

$$+\tilde{\Gamma}^{(2)}_{(03)\,(23)\,(\overline{12})\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(\overline{23})\,(\overline{12})\,(01)} + \tilde{\Gamma}^{(2)}_{(01)\,(13)\,(\overline{12})\,(01)} +$$

$$+\tilde{\Gamma}^{(2)}_{(03)\,(13)\,(\overline{12})\,(01)} + \tilde{\Gamma}^{(2)}_{(03)\,(\overline{13})\,(\overline{12})\,(01)} + \tilde{\Gamma}^{(2)}_{(02)\,(\overline{23})\,(\overline{12})\,(01)}, \qquad (4\text{-}21)$$

where

$$\tilde{\Gamma}^{(2)}_{(02)\,(23)\,(12)\,(01)} = +[f_I^{(0)}(1')f^{(1)}_{I,II'I'}(2')] \quad , \qquad (4\text{-}21a)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(23)\,(12)\,(01)} = +[f_I^{(0)}(1')f^{(1)}_{I,I'II'}(2')] \quad , \qquad (4\text{-}21b)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(\overline{23})\,(12)\,(01)} = -[f_I^{(0)}(1')f^{(1)}_{I,I\ II}(2')] \quad , \qquad (4\text{-}21c)$$

$$\tilde{\Gamma}^{(2)}_{(01)\,(13)\,(12)\,(01)} = +[f^{(1)}_{I,II'I'}(1')f_I^{(0)}(2')] \quad , \qquad (4\text{-}21d)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(13)\,(12)\,(01)} = +[f^{(1)}_{I,I'II'}(1')f_I^{(0)}(2')] \quad , \qquad (4\text{-}21e)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(\overline{13})\,(12)\,(01)} = -[f^{(1)}_{I,I\ II}(1')f_I^{(0)}(2')] \quad , \qquad (4\text{-}21f)$$

$$\tilde{\Gamma}^{(2)}_{(02)\,(\overline{23})\,(12)\,(01)} = -[f_I^{(0)}(1')f^{(1)}_{II,II\ I}(2')] \quad , \qquad (4\text{-}21g)$$

$$\tilde{\Gamma}^{(2)}_{(01)\,(\overline{13})\,(12)\,(01)} = -[f^{(1)}_{II,II\ I}(1')f_I^{(0)}(2')] \quad , \qquad (4\text{-}21h)$$

$$\tilde{\Gamma}^{(2)}_{(02)\,(23)\,(\overline{12})\,(01)} = -[f_I^{(0)}(1)f^{(1)}_{I,II'I'}(2)] \quad , \qquad (4\text{-}21i)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(23)\,(\overline{12})\,(01)} = -[f_I^{(0)}(1)f^{(1)}_{I,I'II'}(2)] \quad , \qquad (4\text{-}21j)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(\overline{23})\,(\overline{12})\,(01)} = +[f_I^{(0)}(1) f^{(1)}_{I,\,I\;II}(2)] \quad , \qquad (4\text{-}21k)$$

$$\tilde{\Gamma}^{(2)}_{(01)\,(13)\,(\overline{12})\,(01)} = -[f^{(1)}_{I,\,II\,I\,'}(1) f_I^{(0)}(2)] \quad , \qquad (4\text{-}21\ell)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(13)\,(\overline{12})\,(01)} = -[f^{(1)}_{I,\,I\,II\,'}(1) f_I^{(0)}(2)] \quad , \qquad (4\text{-}21m)$$

$$\tilde{\Gamma}^{(2)}_{(03)\,(\overline{13})\,(\overline{12})\,(01)} = +[f^{(1)}_{I,\,I\;II}(1) f_I^{(0)}(2)] \quad , \qquad (4\text{-}21n)$$

$$\tilde{\Gamma}^{(2)}_{(02)\,(\overline{23})\,(\overline{12})\,(01)} = +[f_I^{(0)}(1) f^{(1)}_{II,\,II\;I}(2)] \quad , \qquad (4\text{-}21o)$$

We conclude that the coefficient $\tilde{\Gamma}^{(2)}$ is determined by a sum of fifteen collision integrals. They are associated with the diagrams shown in Fig. 3 which represent all of the possible sequences of four successive collisions among three vapor molecules and the droplet. The explicit expressions for these collision integrals are presented in Table II. We note that the signs of the collision integrals depend on whether the number of non-interacting collisions is even or odd.

TABLE II The collision integrals for the coefficient $\tilde{\Gamma}^{(2)}$ of the contribution proportional to n^2 in α.

$$\beta \equiv 4\pi^{-7/2} R^2 m n_\infty \omega_\infty \qquad \int dx_{13} \equiv \int d\vec{\xi}_1 dr_{12} d\vec{\xi}_2 d\hat{\sigma}_{12} dr_{13} d\vec{\xi}_3 d\hat{\sigma}_{13}$$

$$\tilde{\Gamma}^{(2)}_{(02)(23)(12)(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(02)(23)(12)(01)} dx_2' {}_1 \kappa_{12} \kappa_2' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_2''^2}{T^*} + \xi_3''^2)) - \exp(-(\xi_2''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)(23)(12)(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)(23)(12)(01)} dx_2' {}_3 \kappa_{12} \kappa_2' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_2''^2 + \frac{\xi_3''^2}{T^*})) - \exp(-(\xi_2''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)\overline{(23)}(12)(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)\overline{(23)}(12)(01)} dx_2' {}_3 \kappa_{12} \kappa_2' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_2'^2 + \frac{\xi_3^2}{T^*})) - \exp(-(\xi_2'^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(01)(13)(12)(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(01)(13)(12)(01)} dx_1' {}_3 \kappa_{12} \kappa_1' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_1''^2}{T^*} + \xi_3''^2)) - \exp(-(\xi_1''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)(13)(12)(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)(13)(12)(01)} dx_1' {}_3 \kappa_{12} \kappa_1' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_1''^2 + \frac{\xi_3''^2}{T^*})) - \exp(-(\xi_1''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)\overline{(13)}(12)(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)\overline{(13)}(12)(01)} dx_1' {}_3 \kappa_{12} \kappa_1' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_1'^2 + \frac{\xi_3^2}{T^*})) - \exp(-(\xi_1'^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(02)\overline{(23)}(12)(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(02)\overline{(23)}(12)(01)} dx_2' {}_3 \kappa_{12} \kappa_2' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1'^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_2''^2}{T^*} + \xi_3^2)) - \exp(-(\xi_2'^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(01)\overline{(13)}(12)(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(01)\overline{(13)}(12)(01)} dx_1' {}_3 \kappa_{12} \kappa_1' {}_3 \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2'^2)) \left[\frac{n^*}{T^{*3/2}} \exp -(\frac{\xi_1''^2}{T^*} + \xi_3^2)) - \exp(-(\xi_1'^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(02)(23)\overline{(12)}(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(02)(23)\overline{(12)}(01)} dx_{23} \kappa_{12} \kappa_{23} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_2''^2}{T^*} + \xi_3''^2)) - \exp(-(\xi_2''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)(23)\overline{(12)}(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)(23)\overline{(12)}(01)} dx_{23} \kappa_{12} \kappa_{23} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_2''^2 + \frac{\xi_3''^2}{T^*})) - \exp(-(\xi_2''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)\overline{(23)}\overline{(12)}(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)\overline{(23)}\overline{(12)}(01)} dx_{23} \kappa_{12} \kappa_{23} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_2^2 + \frac{\xi_3^2}{T^*})) - \exp(-(\xi_2^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(01)(13)\overline{(12)}(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(01)(13)\overline{(12)}(01)} dx_{13} \kappa_{12} \kappa_{13} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_1''^2}{T^*} + \xi_3''^2)) - \exp(-(\xi_1''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)(13)\overline{(12)}(01)} = +\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)(13)\overline{(12)}(01)} dx_{13} \kappa_{12} \kappa_{13} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_1''^2 + \frac{\xi_3''^2}{T^*})) - \exp(-(\xi_1''^2 + \xi_3''^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(03)\overline{(13)}\overline{(12)}(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(03)\overline{(13)}\overline{(12)}(01)} dx_{13} \kappa_{12} \kappa_{13} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_2^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\xi_1^2 + \frac{\xi_3^2}{T^*})) - \exp(-(\xi_1^2 + \xi_3^2)) \right]$$

$$\tilde{\Gamma}^{(2)}_{(02)\overline{(23)}\overline{(12)}(01)} = -\beta \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_{(02)\overline{(23)}\overline{(12)}(01)} dx_{21} \kappa_{12} \kappa_{21} \, \vec{\xi}_1 \cdot \hat{\sigma} \exp(-(\alpha v r_{12} + \xi_1^2)) \left[\frac{n^*}{T^{*3/2}} \exp(-(\frac{\xi_2^2}{T^*} + \xi_3^2)) - \exp(-(\xi_2^2 + \xi_3^2)) \right]$$

V. Discussion

In this report we have considered an expansion for the mass flux Γ in the nearly free molecular regime having the form:

$$\Gamma = \Gamma^{(0)} + \Gamma^{(1)}\alpha + \tilde{\Gamma}^{(2)}\alpha^2 \ln\alpha + \ldots , \qquad (5\text{-}1)$$

where α is the inverse Knudsen number. The coefficient $\Gamma^{(1)}$ is determined by a set of integrals associated with sequences of collisions among *two* vapor molecules and the droplet. The coefficient $\tilde{\Gamma}^{(2)}$ of the logarithmic term is determined by integrals associated with the asymptotic behavior of collision sequences among *three* vapor molecules and the droplet.

The structure of the expansion (5-1) suggests an analogy with the density dependence of the transport properties of a moderately dense gas. As discussed in an earlier technical report [8], a transport coefficient of a gas, such as the viscosity η, should be written as:

$$\eta = \eta_0 + \eta_1 n + \tilde{\eta}_2 n^2 \ln n + \ldots , \qquad (5\text{-}2)$$

where n is the number density. The value η_0 of the viscosity in the low density limit is given by the Chapman-Enskog theory as an integral over the parameters of a collision between two molecules [13]. The coefficient η_1 of the first density correction involves the effect of

correlations in the position and velocity variables of three molecules. These correlations are of both a statistical and a dynamical nature. The statistical correlations refer to correlations in configuration space irrespective of the velocities of the particles; for a gas of hard spheres they reduce to excluded volume contributions. The dynamical correlations are brought about by sequences of successive collisions; their contribution to η_1 is given by collision integrals associated with three and four successive collisions among three molecules [10].

The sequences of three successive collisions that appear in the calculation of the first correction term η_1 are represented schematically in Fig. 6. In earlier reports [8,10], we have referred to these sequences as a recollision, a cyclic collision and a hypothetical collision. The events indicated by R, C and H in Fig. 2 are obtained from those shown in Fig. 6 when molecule 0 is replaced by the droplet. It appears, therefore, that a close correspondence exists between the two expansions (5-1) and (5-2). The collision sequences to be considered in the evaluation of the coefficients of (5-1) are identical to those previously considered in the density expansion for the transport coefficients if we identify one of the molecules with the droplet. The expansion parameter in (5-2) is actually $n\sigma^3 = \sigma/(n\sigma^2)^{-1}$ which is the ratio of the size σ of the molecules to the mean free

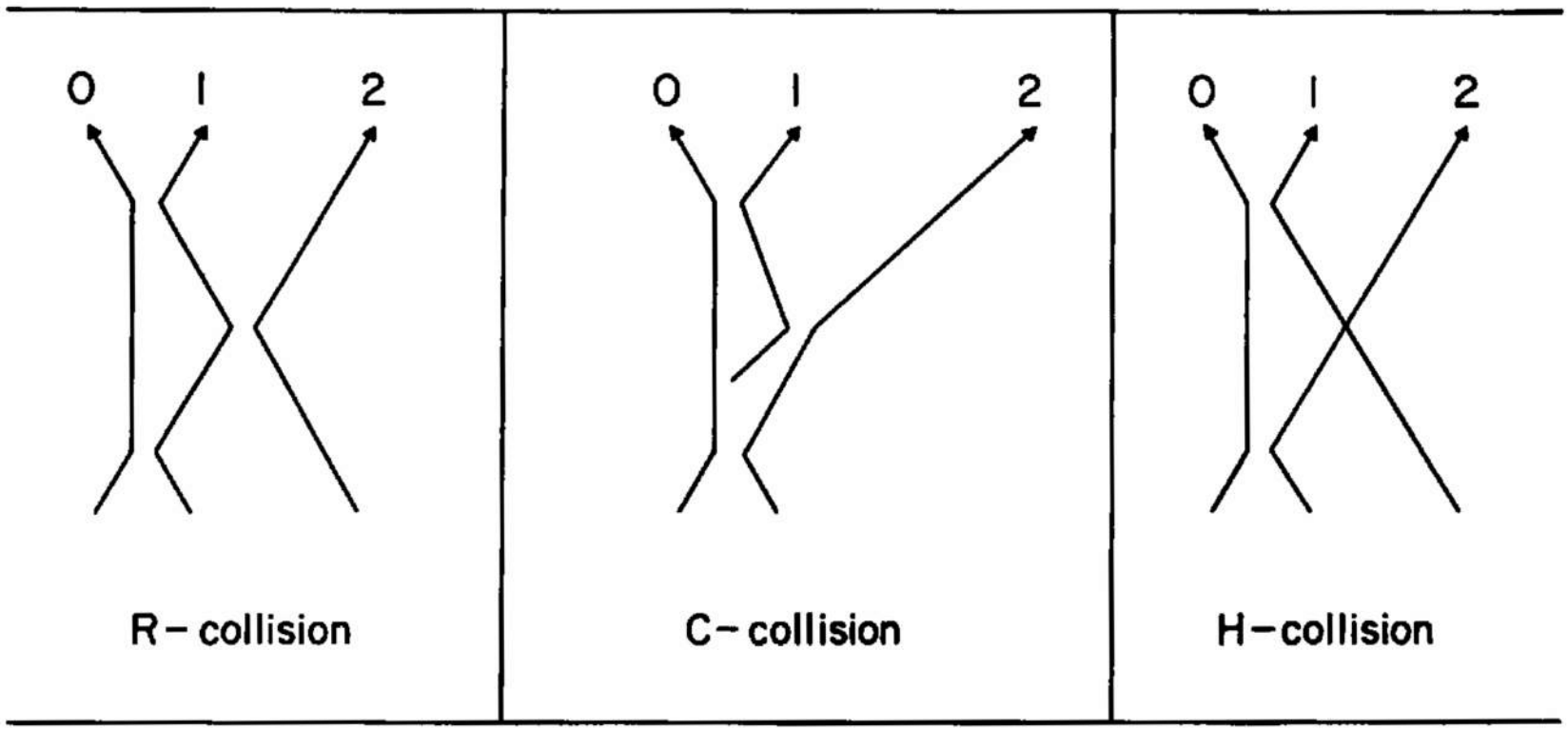

Fig. 6. Sequences of three successive collisions among three molecules that are associated with the first density corrections to the transport properties of a gas [10]. The lines represent schematically the trajectories of molecules 0, 1 and 2.

path ℓ; the expansion parameter in (5-1) is the ratio of the size R of the droplet to the mean free path ℓ.

This correspondence between the density expansion of the transport properties of a gas and the inverse Knudsen number expansion of the properties encountered in rarefied gas dynamics was noted earlier by Dorfman and Sengers [11]. The density expansion (5-2) for the transport properties is obtained by solving the generalized Boltzmann equation. Dorfman et al. have developed from this same equation a theoretical formulation of the aerodynamic forces on an object in a rarefied gas stream by treating the object as a heavy particle [11,12]. Since in our droplet growth problem the number of molecules in the vapor phase is not conserved, we derived the mass flux Γ by solving the inhomogeneous Boltzmann equation subject to the appropriate boundary conditions. While the details of the collision integrals are different, it turns out that the collision sequences we obtained are precisely the same as those derived for the drag coefficient of an object.

Collision integrals determining the first inverse Knudsen number correction to the drag coefficient of a sphere in a gas stream have been calculated by Kuperman and Sengers [21]. The results of these calculations will be reported in a future technical report. It appears that this procedure, with minor modifications, can be adapted to calculate the coefficient $\Gamma^{(1)}$ in (5-1).

APPENDIX A

PHASE SPACE ESTIMATES FOR COLLISION INTEGRALS

In the main text of the report we used the fact that the collision integrals determining the coefficient $\Gamma^{(1)}$ are convergent and that the phase space volumes associated with the collision sequences shown in Fig. 3 diverge logarithmically. Here we discuss the evidence for these assertions. The situation appears to be completely analogous to the phase space volumes of the collision integrals for the transport properties of gases, which were analyzed by Dorfman and Cohen [16]. In order not to prejudice the result by this analogy, however, we have made an independent study of the collision integrals derived in this report. A similar analysis of the collision integrals for the Knudsen number dependence of the force on a macroscopic object in a rarefied gas was made by McClure and Dorfman [12].

In order to make an estimate of the phase space volumes associated with the collision integrals for $\Gamma^{(1)}$, we consider as an example the recollision contribution:

$$\Gamma_R^{(1)} = -4\pi^{-2}R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_{(R)} d\vec{\xi}_1 d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \vec{\xi}_1 \cdot \hat{\rho}$$

$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\{-(\frac{\xi_1'^2}{T^*} + \xi_2'^2)\} - \exp\{-(\xi_1'^2 + \xi_2'^2)\} \right]. \quad \text{(A-1)}$$

Since the integrals over the velocities $\vec{\xi}_1$ and $\vec{\xi}_2$ are well

behaved as a result of the presence of the exponential factors, the convergence of $\Gamma_R^{(1)}$ depends upon the behavior of the τ_{12} and $\hat{\sigma}_{12}$-integrations for large values of τ_{12}. It is convenient to change the sign of the velocities $\vec{\xi}_1$ and $\vec{\xi}_2$ and to consider the recollision event of Fig. 2 with the direction of motion of molecules 1 and 2 reversed. Let us choose a coordinate system in which molecule 1 is at rest at the origin just prior to the (12) collision and in which the Z-axis is taken in the direction of $-\vec{\xi}_1$ (see Fig. 7). The droplet is then moving in the Z-direction and, at the time of the (12) collision ($\tau=\tau_{12}$), its center is located at $\vec{r} = -\hat{\rho}-\vec{\xi}_1\tau_{12} \simeq -\vec{\xi}_1\tau_{12}$ for large values of τ_{12}. After the (12) collision, molecule 1 moves in this coordinate system in the direction of $\hat{\sigma}_{12}$ with a velocity $\vec{\xi}_{1'1} \equiv \vec{\xi}_1'-\vec{\xi}_1$. In order for 1 to catch up with the droplet, the perihelion vector $\hat{\sigma}_{12}$ must be restricted to a solid angle proportional to $r^{-2} \simeq |\vec{\xi}_1\tau_{12}|^{-2}$. Thus the phase space volume behaves for large values of τ_{12} as:

$$\int d\tau_{12} \int_{(R)} d\hat{\sigma}_{12} \sim \int d\tau_{12} \frac{1}{\tau_{12}^2} , \qquad \text{(A-2)}$$

which is clearly convergent when the upper limit of integration goes to infinity.

The integrals $\Gamma_C^{(1)}$ and $\Gamma_H^{(1)}$ also involve three successive collisions and exhibit the same asymptotic behavior

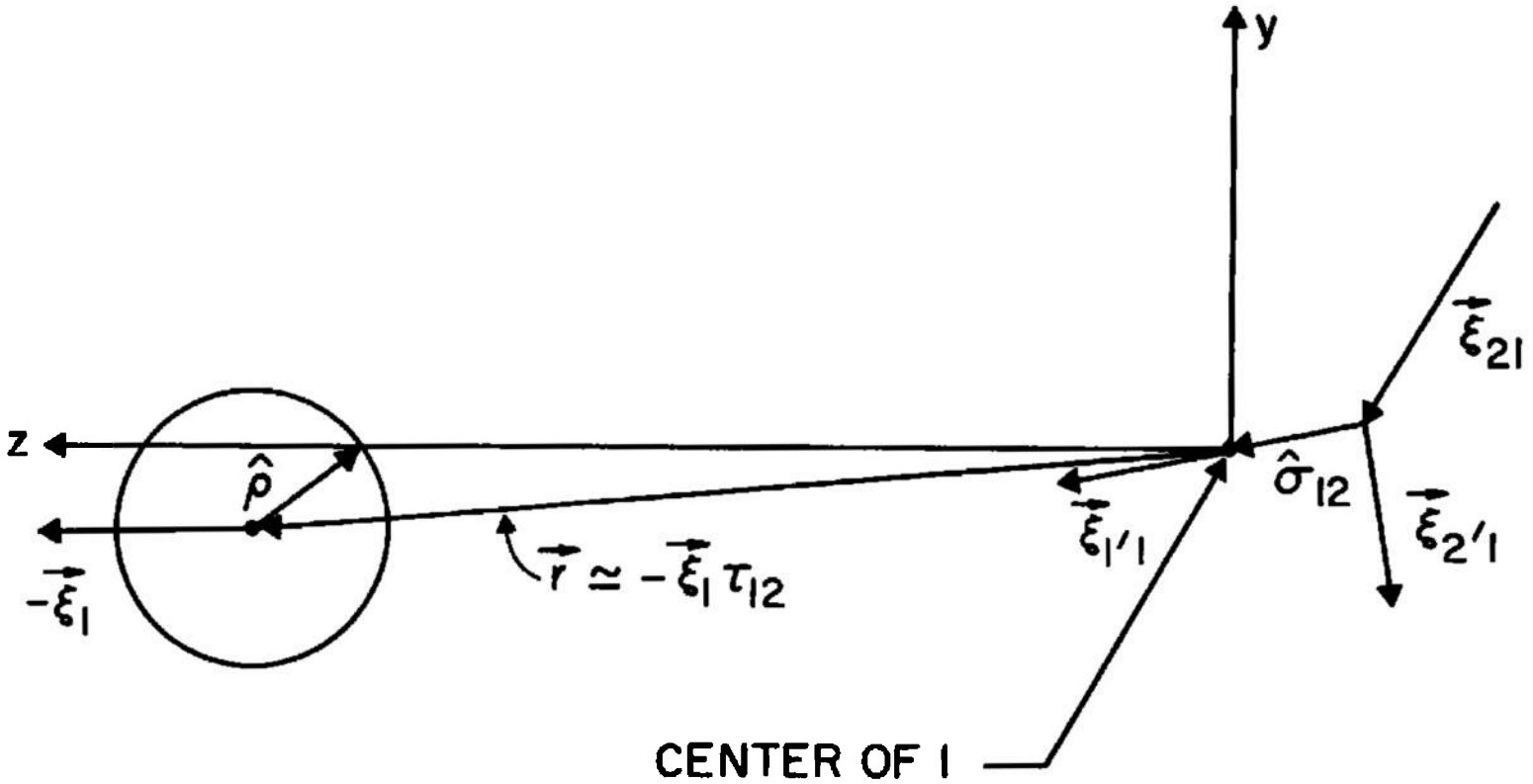

Fig. 7. Coordinate system for the recollision sequence.

as $\Gamma_R^{(1)}$. The collision integral $\Gamma_{RC}^{(1)}$ requires the occurrence of an additional collision and, therefore, converges even more rapidly. In fact, it turns out that the RC-collision sequence is only possible when the (12) collision takes place close to the droplet.

We next evaluate the phase space volumes associated with the sequences of four collisions among three vapor molecules and the droplet shown in Fig. 3. As an example we consider the term:

$$\Gamma^{(2)}_{(02)\,(23)\,(12)\,(01)} = -4\pi^{-\frac{7}{2}} R^2 m n_\infty \omega_\infty \int_0^\infty d\tau_{12} \int_0^\infty d\tau_{2'3} \int_{(02)\,(23)\,(12)\,(01)} d\vec{\xi}_1 d\vec{\xi}_2 d\vec{\xi}_3 d\hat{\sigma}_{12} d\hat{\sigma}_{2'3}$$

$$\cdot \kappa_{12}\kappa_{2'3} \vec{\xi}_1 \cdot \hat{\rho}\, \exp(-\xi_1'^2) \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{ -\left(\frac{\xi_2''^2}{T^*} + \xi_3''^2 \right) \right\} - \right.$$

$$\left. - \exp\left\{ -\left(\xi_2''^2 + \xi_3''^2 \right) \right\} \right] , \qquad \text{(A-3)}$$

which corresponds to the diagram in Fig. 4 and is one of the terms contributing to (4-5).

For the discussion, we again change the signs of the velocities so as to reverse the direction of motion of the vapor molecules in Fig. 4. Thus $\vec{\xi}_1, \vec{\xi}_2, \vec{\xi}_3$ now refer

to the initial velocities, $\vec{\xi}_1', \vec{\xi}_2', \vec{\xi}_3'$ ($\vec{\xi}_3' = \vec{\xi}_3$) to the velocities after the (12) collision and $\vec{\xi}_1'', \vec{\xi}_2'', \vec{\xi}_3''$ to the velocities after the (23) collision.

We take a coordinate system in which molecule 2 is at rest at the origin just prior to the (23) collision and the Z-axis is in the direction of $-\vec{\xi}_2'$ (see Fig. 8). The velocities of the molecules in this coordinate system are at various times: $\vec{\xi}_{i2'} = \vec{\xi}_i - \vec{\xi}_2'$, $\vec{\xi}_{i'2'} = \vec{\xi}_i' - \vec{\xi}_2'$ and $\vec{\xi}_{i''2'} = \vec{\xi}_i'' - \vec{\xi}_2'$ ($i = 1,2,3$). The center of the droplet at the time of the (23) collision ($\tau = \tau_{12} + \tau_{2'3}$) is located at $\vec{r} = -\hat{\rho} - \vec{\xi}_1\tau_{12} - \vec{\xi}_2'\tau_{2'3} \simeq -\vec{\xi}_1\tau_{12} - \vec{\xi}_2'\tau_{2'3}$ for large values of τ_{12}. After the (23) collision molecule 2 will move in the direction of $\hat{\delta}_{2'3}$ with a velocity $\vec{\xi}_{2''2'}$. In order for molecule 2 to catch up with the droplet, the perihelion vector must be restricted to a solid angle proportional to $r^{-2} \simeq |\vec{\xi}_1\tau_{12} + \vec{\xi}_2'\tau_{2'3}|^{-2}$. Then the phase space volume behaves as:

$$\int d\tau_{12} d\tau_{2'3} \int d\hat{\delta}_{2'3} \sim \int d\tau_{12} d\tau_{2'3} |\vec{\xi}_1\tau_{12} + \vec{\xi}_2'\tau_{2'3}|^{-2} \qquad \text{(A-4)}$$

(02) (23) (12) (01)

which diverges as:

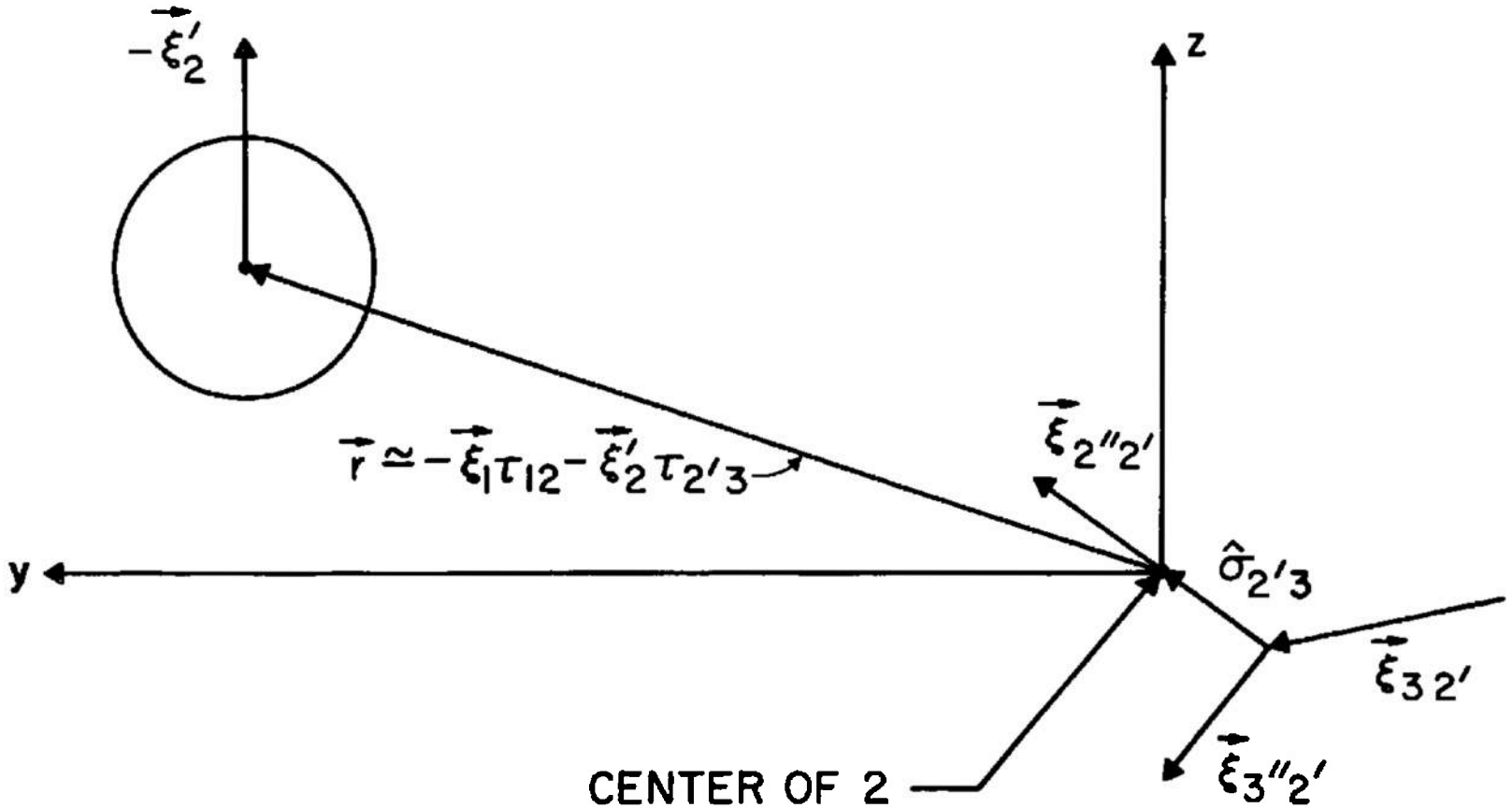

Fig. 8. Coordinate system for the (02)(23)(12)(01) collision sequence.

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$$\lim_{T\to\infty} \int^{T} \frac{d\tau_{12}}{\tau_{12}} = \lim_{T\to\infty} \ln T. \qquad \text{(A-5)}$$

The phase space volumes associated with the other collision sequences of Fig. 3 also require the occurrence of four successive collisions and therefore exhibits the same behavior at a function of τ_{12}.

In addition we encountered sequences of five or more collisions among three molecules and the droplet. However, because of the severe restrictions resulting from the required occurrence of the fifth collision, it turns out that the corresponding integrands fall off at least as fast as τ_{12}^{-2}. Thus the phase space volumes of these dynamically more complicated collision sequences are finite.

APPENDIX B

ANALYSIS OF HIGHER ORDER TERMS

In Section IV we considered an expansion for the distribution function:

$$f(\vec{\rho},\vec{\xi}) = f^{(0)}(\vec{\rho},\vec{\xi}) + f^{(1)}(\vec{\rho},\vec{\xi}) + f^{(2)}(\vec{\rho},\vec{\xi}) + \ldots, \quad \text{(B-1)}$$

where $f^{(2)}(\vec{\rho},\vec{\xi})$ should satisfy equation (4-2). For convenience, we rewrite this equation as:

$$\vec{\xi}_1 \cdot \frac{\partial f^{(2)}(\vec{\rho},\vec{\xi}_1)}{\partial \vec{\rho}} = \alpha \int d\vec{\xi}_2 d\hat{\sigma}_{12} \kappa_{12} \left[S_1(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) - f^{(2)}(\vec{\rho},\vec{\xi}_1) f_\infty(\xi_2) + \right.$$

$$\left. + S_2(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) + S_3(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) \right], \quad \text{(B-2)}$$

where

$$S_1(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) \equiv f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(1)}(\vec{\rho},\vec{\xi}_2') + f^{(1)}(\vec{\rho},\vec{\xi}_1') f^{(0)}(\vec{\rho},\vec{\xi}_2') +$$

$$- f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(1)}(\vec{\rho},\vec{\xi}_2) - f^{(1)}(\vec{\rho},\vec{\xi}_1) f^{(0)}(\vec{\rho},\vec{\xi}_2),$$

(B-2a)

$$S_2(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) \equiv f^{(0)}(\vec{\rho},\vec{\xi}_1') f^{(2)}(\vec{\rho},\vec{\xi}_2') + f^{(2)}(\vec{\rho},\vec{\xi}_1') f^{(0)}(\vec{\rho},\vec{\xi}_2') +$$

$$- f^{(0)}(\vec{\rho},\vec{\xi}_1) f^{(2)}(\vec{\rho},\vec{\xi}_2) - f^{(2)}(\vec{\rho},\vec{\xi}_1) g(\vec{\rho},\vec{\xi}_2),$$

(B-2b)

with $$g(\vec{\rho},\vec{\xi}) \equiv f^{(0)}(\vec{\rho},\vec{\xi}) - f_{\infty}(\xi),$$

and

$$S_3(\vec{\rho},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) \equiv f^{(1)}(\vec{\rho},\vec{\xi}_1')f^{(1)}(\vec{\rho},\vec{\xi}_2') - f^{(1)}(\vec{\rho},\vec{\xi}_1)f^{(1)}(\vec{\rho},\vec{\xi}_2).$$

This equation can be written in integral form as:

$$f^{(2)}(\vec{\rho},\vec{\xi}_1) = \tilde{f}^{(2)}(\vec{\rho},\vec{\xi}_1) + \alpha\int_0^t d\tau_{12}\int d\vec{\xi}_2 d\hat{\sigma}_{12}\kappa_{12}e^{-\alpha\nu(\xi_1)\tau_{12}}$$

$$\cdot[S_2(\vec{\rho}-\vec{\xi}_1\tau_{12},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2) + S_3(\vec{\rho}-\vec{\xi}_1\tau_{12},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2)], \tag{B-3}$$

where

$$\tilde{f}^{(2)}(\vec{\rho},\vec{\xi}_1) \equiv \alpha\int_0^t d\tau_{12}\int d\vec{\xi}_2 d\hat{\sigma}_{12}\kappa_{12}e^{-\alpha\nu(\xi_1)\tau_{12}}\ S_1(\vec{\rho}-\vec{\xi}_1\tau_{12},\hat{\sigma}_{12},\vec{\xi}_1,\vec{\xi}_2), \tag{B-4}$$

and the upper limit t of the τ_{12}-integration is again given by (3-4).

In deriving the contribution to the mass flux proportional to $\alpha^2\ln\alpha$ we neglected the terms S_2 and S_3 in (B-2). We thus identified $f^{(2)}(\vec{\rho},\vec{\xi}_1)$ in (4-9) with the first term $\tilde{f}^{(2)}(\vec{\rho},\vec{\xi}_1)$ of (B-3) and assumed that the other term in (B-3) would not modify the coefficient of this

logarithmic term. In this Appendix we shall discuss the evidence for this assertion. For this purpose we shall show that the correction term to $\tilde{f}^{(2)}(\vec{\rho},\vec{\xi}_1)$, as given by (B-3), leads to contributions to the mass flux Γ that are of order higher than $\alpha^2 \ln\alpha$. The mathematical assumption implicit in this procedure will be discussed at the end of this Appendix.

The correction term to $\tilde{f}^{(2)}(\vec{\rho},\vec{\xi})$ is obtained by iterating (B-3) once; that is, we approximate $f^{(2)}(\vec{\rho},\vec{\xi})$ in the S_2 term by $\tilde{f}^{(2)}(\vec{\rho},\vec{\xi})$. This then gives for the $\alpha^2 \ln\alpha$ contribution to the mass flux Γ:

$$-4\pi R^2 m n_\infty \omega_\infty \lim_{\alpha\to 0} \frac{1}{\alpha^2 \ln\alpha} \int_{\vec{\xi}_1\cdot\hat{\rho}<0} d\vec{\xi}_1 \vec{\xi}_1\cdot\hat{\rho}\; f^{(2)}(\hat{\rho},\vec{\xi}_1) =$$

$$= \tilde{\Gamma}^{(2)} + \delta\tilde{\Gamma}^{(2)} \quad . \tag{B-5}$$

Here $\tilde{\Gamma}^{(2)}$ is the contribution to the mass flux from $\tilde{f}^{(2)}(\vec{\rho},\vec{\xi})$ and is precisely the coefficient in (4-12). The correction term $\delta\tilde{\Gamma}^{(2)}$ may be written as:

$$\delta\tilde{\Gamma}^{(2)} = \delta\tilde{\Gamma}_1^{(2)} + \delta\tilde{\Gamma}_2^{(2)} \quad , \tag{B-6}$$

where

$$\delta\tilde{\Gamma}_1^{(2)} \equiv \left[f^{(0)}(1')\tilde{f}^{(2)}(2')\right] + \left[\tilde{f}^{(2)}(1')f^{(0)}(2')\right] + - \left[f^{(0)}(1)\ \tilde{f}^{(2)}(2)\ \right] - \left[\tilde{f}^{(2)}(1)\ g(2)\ \right], \quad \text{(B-6a)}$$

$$\delta\tilde{\Gamma}_2^{(2)} \equiv \left[f^{(1)}(1')f^{(1)}(2')\right] - \left[f^{(1)}(1)\ f^{(1)}(2)\ \right], \quad \text{(B-6b)}$$

and we have again used the shorthand notation introduced in (4-13). It remains our task to show that $\delta\tilde{\Gamma}_1^{(2)}$ and $\delta\tilde{\Gamma}_2^{(2)}$ vanish due to the limit $\alpha\to 0$ contained in these terms.

Considering first the $\delta\tilde{\Gamma}_1^{(2)}$ term, we decompose $\tilde{f}^{(2)}$ to obtain:

$$\tilde{f}^{(2)}(\vec{\rho},\vec{\xi}_i) = \tilde{f}_I^{(2)}(\vec{\rho},\vec{\xi}_i) + \tilde{f}_{II}^{(2)}(\vec{\rho},\vec{\xi}_i), \quad \text{(B-7)}$$

where

$$\tilde{f}_I^{(2)}(\vec{\rho},\vec{\xi}_i) \equiv \begin{cases} \alpha\int_0^t d\tau_{i3}\int d\vec{\xi}_3 d\hat{\sigma}_{i3}\kappa_{i3} e^{-\alpha\nu(\xi_i)\tau_{i3}}\ S_1(\vec{\rho}-\vec{\xi}_i\tau_{i3},\hat{\sigma}_{i3},\vec{\xi}_i,\vec{\xi}_3) \\ \qquad\qquad \text{for } \vec{\xi}_i \in I(\rho), \\ 0 \qquad\qquad \text{for } \vec{\xi}_i \in II(\rho) \end{cases} \quad \text{(B-7a)}$$

$$\tilde{f}_{II}^{(2)}(\vec{\rho},\vec{\xi}_i) \equiv \begin{cases} \alpha\int_0^{T(\vec{\rho},\vec{\xi}_i)} d\tau_{i3}\int d\vec{\xi}_3 d\hat{\sigma}_{i3}\kappa_{i3} e^{-\alpha\nu(\xi_i)\tau_{i3}}\ S_1(\vec{\rho}-\vec{\xi}_i\tau_{i3},\hat{\sigma}_{i3},\vec{\xi}_i,\vec{\xi}_3) \\ \qquad\qquad \text{for } \vec{\xi}_i \in II(\rho), \\ 0 \qquad\qquad \text{for } \vec{\xi}_i \in I(\rho). \end{cases} \quad \text{(B-7b)}$$

and $T(\vec{\rho},\vec{\xi}_i)$ is given by (3-5). We thus have in analogy to (4-15):

$$\delta\tilde{\Gamma}_1^{(2)} = \left[f_I^{(0)}(1')\tilde{f}_I^{(2)}(2') \right] + \left[\tilde{f}_I^{(2)}(1') f_I^{(0)}(2') \right] + \left[f_I^{(0)}(1')\tilde{f}_{II}^{(2)}(2') \right] +$$
$$+ \left[\tilde{f}_I^{(2)}(1') f_{II}^{(0)}(2') \right] + \left[f_{II}^{(0)}(1')\tilde{f}_I^{(2)}(2') \right] + \left[\tilde{f}_{II}^{(2)}(1') f_I^{(0)}(2') \right] +$$
$$+ \left[f_{II}^{(0)}(1')\tilde{f}_{II}^{(2)}(2') \right] + \left[\tilde{f}_{II}^{(2)}(1') f_{II}^{(0)}(2') \right] - \left[f_I^{(0)}(1)\tilde{f}_I^{(2)}(2) \right] +$$
$$- \left[f_I^{(0)}(1)\tilde{f}_{II}^{(2)}(2) \right] - \left[\tilde{f}_I^{(2)}(1) g_{II}(2) \right] , \qquad \text{(B-8)}$$

where $g_{II}(2) \equiv g(2)$ gives only a contribution when $\vec{\xi}_2 \epsilon II(|\hat{\rho}-\vec{\xi}_1 \tau_{12}|)$. If we now substitute $f^{(0)} = f_I^{(0)} + f_{II}^{(0)}$ and $f^{(1)} = f_I^{(1)} + f_{II}^{(1)}$, as given by (2-14) and (3-6), into (B-7a) and (B-7b), and then in turn substitute (B-7a) and (B-7b) into (B-8), we find that $\delta\tilde{\Gamma}_1^{(2)}$ is given by a sum of integrals. Each of these integrals is associated with a collision sequence involving five or more collisions among *four* molecules and the droplet. The leading contribution is determined by those integrals that are related to sequences of five successive collisions; these sequences are presented in Table III.

As an example we consider the collision sequence (03) (34) (13) (12) (01) which is schematically represented in Fig. 9. The contribution from this event to $\delta\tilde{\Gamma}_1^{(2)}$ is given by:

TABLE III Sequences of five successive collisions among four molecules and the droplet associated with $\delta\tilde{\Gamma}_1^{(2)}$.

Term in (B.6)	Collision sequences		
$-\left[f_I^{(0)}(1') \tilde{f}_I^{(2)}(2')\right]$	(03)(34)(23)(12)(01)	(04)($\overline{24}$)(23)(12)(01)	(04)($\overline{34}$)($\overline{23}$)(12)(01)
	(04)(34)(23)(12)(01)	(03)($\overline{34}$)(23)(12)(01)	(02)(24)($\overline{23}$)(12)(01)
	(04)($\overline{34}$)(23)(12)(01)	(02)($\overline{24}$)(23)(12)(01)	(04)(24)($\overline{23}$)(12)(01)
	(02)(24)(23)(12)(01)	(03)(34)($\overline{23}$)(12)(01)	(04)($\overline{24}$)($\overline{23}$)(12)(01)
	(04)(24)(23)(12)(01)	(04)(34)($\overline{23}$)(12)(01)	(03)($\overline{34}$)($\overline{23}$)(12)(01)
$\left[\tilde{f}_I^{(2)}(1') f_I^{(0)}(2')\right]$	(03)(34)(13)(12)(01)	(04)($\overline{14}$)(13)(12)(01)	(04)($\overline{34}$)($\overline{13}$)(12)(01)
	(04)(34)(13)(12)(01)	(03)($\overline{34}$)(13)(12)(01)	(01)(14)($\overline{13}$)(12)(01)
	(04)($\overline{34}$)(13)(12)(01)	(01)($\overline{14}$)(13)(12)(01)	(04)(14)($\overline{13}$)(12)(01)
	(01)(14)(13)(12)(01)	(03)(34)($\overline{13}$)(12)(01)	(04)($\overline{14}$)($\overline{13}$)(12)(01)
	(04)(14)(13)(12)(01)	(04)(34)($\overline{13}$)(12)(01)	(03)($\overline{34}$)($\overline{13}$)(12)(01)
$\left[f_I^{(0)}(1) \tilde{f}_I^{(2)}(2)\right]$	(03)(34)(23)($\overline{12}$)(01)	(04)($\overline{24}$)(23)($\overline{12}$)(01)	(04)($\overline{34}$)($\overline{23}$)($\overline{12}$)(01)
	(04)(34)(23)($\overline{12}$)(01)	(03)($\overline{34}$)(23)($\overline{12}$)(01)	(02)(24)($\overline{23}$)($\overline{12}$)(01)
	(04)($\overline{34}$)(13)($\overline{12}$)(01)	(02)($\overline{24}$)(23)($\overline{12}$)(01)	(04)(24)($\overline{23}$)($\overline{12}$)(01)
	(02)(24)(23)($\overline{12}$)(01)	(03)(34)($\overline{23}$)($\overline{12}$)(01)	(04)($\overline{24}$)($\overline{23}$)($\overline{12}$)(01)
	(04)(24)(23)($\overline{12}$)(01)	(04)(34)($\overline{23}$)($\overline{12}$)(01)	(03)($\overline{34}$)($\overline{23}$)($\overline{12}$)(01)
$\left[f_I^{(0)}(1') \tilde{f}_{II}^{(2)}(2')\right]$		(02)($\overline{24}$)($\overline{23}$)(12)(01)	
$\left[\tilde{f}_{II}^{(2)}(1') f_I^{(0)}(2')\right]$		(01)($\overline{14}$)($\overline{13}$)(12)(01)	
$\left[f_I^{(0)}(1) \tilde{f}_{II}^{(2)}(2)\right]$		(02)($\overline{24}$)($\overline{23}$)($\overline{12}$)(01)	

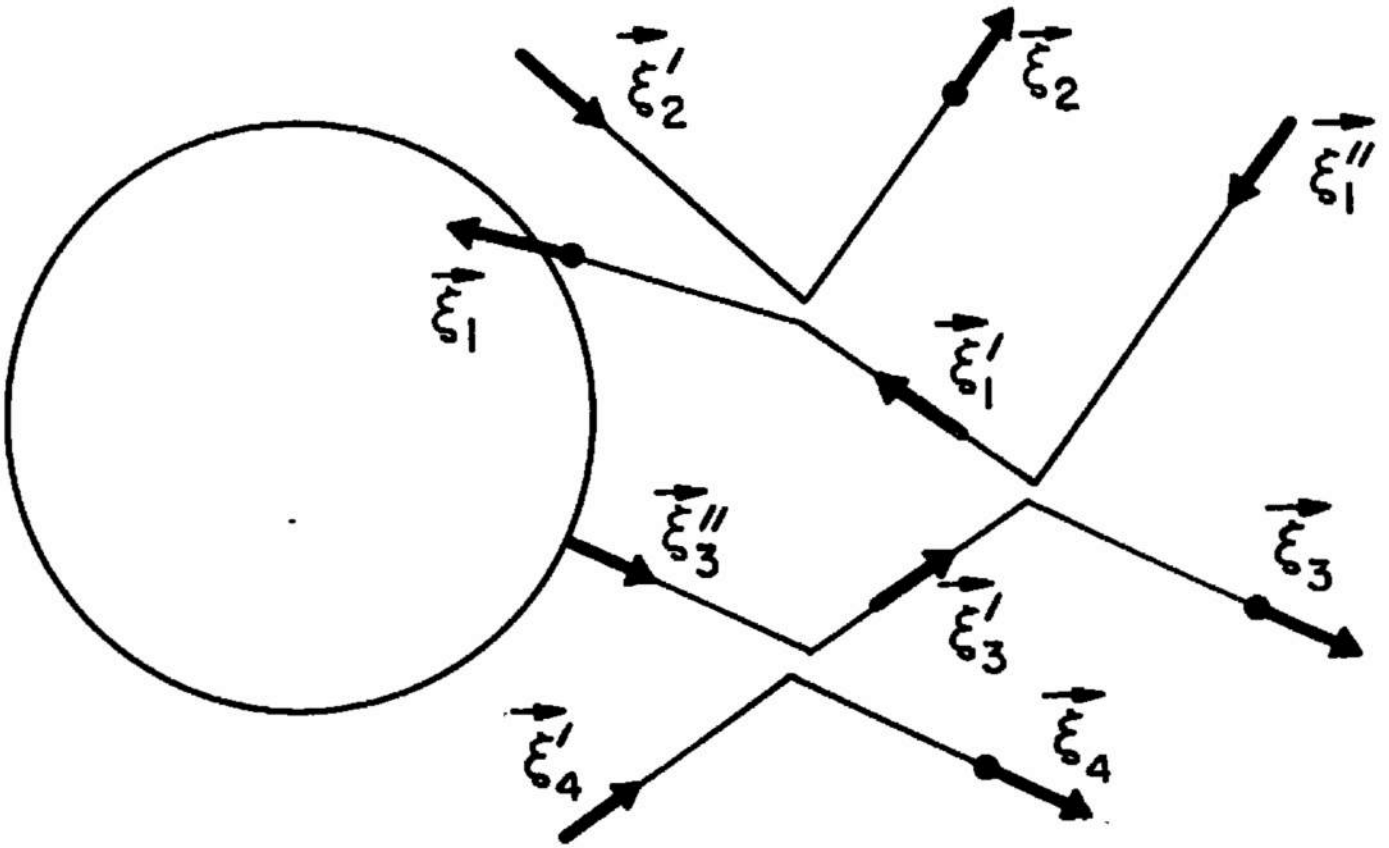

Fig. 9. Example of a sequence of five collisions among four vapor molecules and the droplet.

$$\delta\tilde{\Gamma}^{(2)}_{(03)(34)(13)(12)(01)} = -4\pi^{-5}R^2 mn_\infty \omega_\infty \lim_{\alpha\to 0} \frac{\alpha}{\ln\alpha}$$

$$\cdot \int_0^\infty d\tau_{12} \int_0^\infty d\tau_{1'3} \int_0^\infty d\tau_{3'4} \int d\vec{\xi}_1 d\vec{\xi}_2 d\hat{\sigma}_{12} d\vec{\xi}_3 d\hat{\sigma}_{1'3} d\vec{\xi}_4 d\hat{\sigma}_{3'4}$$

$$\cdot \kappa_{12}\kappa_{1'3}\kappa_{3'4} \vec{\xi}_1 \cdot \hat{\rho} \exp\{-\alpha\nu(\tau_{12}+\tau_{1'3})\} \exp\{-(\xi_2'^2+\xi_1''^2)\}$$

$$\cdot \left[\frac{n^*}{T^{*\frac{3}{2}}} \exp\left\{-\left(\frac{\xi_3''^2}{T^*} + \xi_4'^2\right)\right\} - \exp\left\{-(\xi_3''^2 + \xi_4'^2)\right\}\right] , \qquad \text{(B-9)}$$

where we have replaced $\nu(\xi_1)$ and $\nu(\xi_1')$ by the constant ν since this change will not affect the result. The meaning of the velocities $\vec{\xi}_i, \vec{\xi}_1'$ and $\vec{\xi}_i''$ is explained in Fig. 9. The symbols τ_{ij}, $\hat{\sigma}_{ij}$ and κ_{ij} refer to the collision that produces the velocities $\vec{\xi}_i$ and $\vec{\xi}_j$. In order to study the behavior in the limit $\alpha\to 0$, we need to estimate the phase space for large values of τ_1 and $\tau_{1'3}$. Using the same arguments as in Appendix A it is evident that $\hat{\sigma}_{3'4}$ is restricted to a solid angle proportional to $|\vec{\xi}_1\tau_{12} + \vec{\xi}_1'\tau_{1'3} + \vec{\xi}_3'\tau_{3'4}|^{-2}$. After carrying out the

integration over $\tau_{3'4}$, the integrand will be proportional to $|\vec{\xi}_1\tau_{12} + \vec{\xi}_1'\tau_{1'3}|^{-1}$. Thus the asymptotic behavior of the integrand is determined by an integral of the type:

$$I = \lim_{\alpha\to 0} \frac{\alpha}{\ln\alpha} \int_0^\infty d\tau_{12} \int_0^\infty d\tau_{1'3} \frac{e^{-\alpha\nu(\tau_{12} + \tau_{1'3})}}{|\vec{\xi}_1\tau_{12} + \vec{\xi}_1'\tau_{1'3}|} \quad . \tag{B-10}$$

Using the coordinate transform $x = \alpha\nu\tau_{12}$ and $y = \alpha\nu\tau_{1'3}$, we see that:

$$I \equiv \frac{1}{\nu} \lim_{\alpha\to 0} \frac{1}{\ln\alpha} \int_0^\infty dx \int_0^\infty dy \frac{e^{-(x+y)}}{|\vec{\xi}_1 x + \vec{\xi}_1' y|} \quad , \tag{B-11}$$

which vanishes in the limit $\alpha \to 0$. Similar arguments can be used to show that the contribution to (B-6) from all sequences in Table III vanishes in the limit $\alpha \to 0$.

If we next consider the term $\delta\tilde{\Gamma}_2^{(2)}$ in (B-6b), we find that it may also be decomposed into a sum of integrals, each of which may be associated with a collision sequence. These collision sequences, however, involve six or more collisions among four molecules and the droplet. The phase space volumes associated with these sequences are thus smaller than those associated with the sequences in Table III and $\delta\tilde{\Gamma}_2^{(2)}$ will likewise be zero.

In the main body of this report we extracted from equation (4-2) an $\alpha^2\ln\alpha$ contribution to the mass flux Γ and determined its coefficient $\tilde{\Gamma}^{(2)}$. In this Appendix,

we have demonstrated that the leading contributions from the terms neglected are of higher order in α and do not modify $\tilde{\Gamma}^{(2)}$. A completely rigorous proof of this logarithmic term, however, should consider all of the higher order terms and show that their sum is also of higher order than $\alpha^2 \ln\alpha$. For that purpose we would not only need the solution of (4-2) to all orders in α, but also the sum of the higher order terms in (4-1). In this respect, the situation is again analogous to the density dependence of the transport properties of gases. For a three dimensional gas a resummation of the most divergent terms encountered in a formal power series expansion in the density n leads to the $n^2 \ln n$ term in (5-2) with a finite coefficient $\tilde{\eta}_2$ [16, 20,22]. Again for a rigorous proof one would have to show that a resummation over all the less divergent terms would not change this result. Such a complete proof is not yet available for the density dependence of the transport properties, nor for the Knudsen number dependence of the mass flux considered in this report.

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13. ABSTRACT

A method is developed for calculating the mass flux to a liquid droplet surrounded by its pure vapor as a function of the Knudsen number. The Knudsen number K is defined as the ratio of the mean free path to the droplet size. When the mass flux is expanded in terms of the inverse Knudsen number $\alpha = K^{-1}$, we obtain a series of the form $\Gamma = \Gamma^{(0)} + \Gamma^{(1)}\alpha + \tilde{\Gamma}^{(2)}\alpha^2 \ln\alpha + \ldots$. It is shown that the coefficients are determined by integrals associated with sequences of successive collisions among a number of vapor molecules and the droplet. In particular, we derive the collision integrals for the first three coefficients of the inverse Knudsen number expansion for Γ. These collision integrals bear a close similarity to the collision integrals derived in earlier technical reports for the density dependence of the transport properties of gases. It will be demonstrated in a subsequent technical report that the same method can be used to calculate the aerodynamic force on an object in a gas stream as a function of the Knudsen number.

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1. Knudsen flow						
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drops (liquids)						
particle collisions						
vapor						
supersaturation						
condensation						
nucleation						
2. Droplets -- Growth						
3. Supersaturated vapor.						

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